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FIELD MEASUREMENT AND MODEL EVALUATION
PROGRAM FOR ASSESSMENT OF THE ENVIRONMENTAL
EFFECTS OF MILITARY SMOKES

OIL ANALYSIS METHOD FOR STUDY OF ATMOSPHERIC DISPERSION OF MILITARY FOG OIL SMOKES

FINAL REPORT

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Methods for sampling and analysis of U.S. Army SGF-2 fog oil smoke from an Army M3A3 or M3A4 smoke generator are developed. This includes sampling of the aerosol and vapor fractions of the smoke, and development of a heat desorption - gas chromatographic method for sample analysis. An investigation of the accuracy of the method in estimating field concentrations is also presented.

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EXECUTIVE SUMMARY

An improved method for analysis of fog oil samples of both aerosol and vapor from field dispersion experiments is described. The intent of this method is to maintain the accuracy and sensitivity of earlier procedures while reducing the analysis time and the time required for manual preparation of the samples before analysis.

In this method fog-oil is vaporized from a sample using heat, then the hot vapor is analyzed by gas chromatography. A non-polar packed column, which can tolerate a wide range in sample mass loadings, is used for separation of the fog-oil chemical constituents. A flame ionization detector is used to determine the total sample mass. A sensitivity of 0.03 mg has been achieved, and samples up to 20 mg can be analyzed easily.

Chromatograms produced using this method give a qualitative molecular weight distribution of the oil. Similar chromatograms are generated with ASTM method 2887 for petroleum fractions and ASTM method 3710 for gasoline fractions. Better resolution of the chemical constituents may be achieved using a capillary column or an open tubular column. We do not use these higher resolution columns because of overloading problems associated with analyzing samples of unknown mass.

Fog oil smoke is produced by vaporizing the liquid oil in the engine manifold of a thermal smoke generator. Upon mixing into the atmosphere, the vapor forms small aerosol droplets. Glass fiber filters are used for sampling the aerosol fraction of the smoke. Stainless steel tubes filled with Tenax-GC are used for sampling the vapor fraction of the oil. In laboratory and field experiments, we have found that very little of the relatively nonvolatile oil exists as a vapor at distances from the source and at the concentrations we are measuring.

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1.0 INTRODUCTION

The purpose of this paper is to discuss the development of a sampling and analysis method for fog-oil smoke. This method is needed as part of a larger project for field measurements of smoke concentration in atmospheric dispersion experiments using fog-oil smoke.

1.1 Sampling Methods for Air Pollution and Atmospheric Tracers

Knowledge of the atmospheric concentration and deposition of wind carried pollutants is important for determining their effect on plants, animals and people. Accurate measurements of pollutants and tracers introduced into the atmosphere are needed to validate and refine models of atmospheric dispersion and evaluate pollution-related health effects. This paper concentrates on finding and developing new sampling and analysis techniques for a fog-oil smoke.

Methods used for sampling pollution and atmospheric tracers are investigated and adapted for this application. Pollutants carried in the atmosphere consist of particulates, vapors, and gases. The appropriate sampling method depends on the nature of the pollutant. Particulates are generally collected using filters, impactors, impingers or cyclones. Vapors and gases may be collected using bubblers, cryogenic traps, or solid adsorbents. Fog-oil smoke is a condensation aerosol which exists as a two phase mixture of micron size liquid droplets and vapor. This increases the problems associated with taking valid atmospheric samples and interpretation of the analytical results. The primary goal of the present study is to develop a method for sampling, analyzing, and quantifying the total mass fraction of fog-oil smoke downwind of a smoke generator. An investigation of the vapor and particulate relationship is also needed as well as information on gross chemical composition and aerosol size distribution.

1.2 Field Experiments on Fog Oil

We have measured the atmospheric concentration of a fog-oil smoke downwind of a fog-oil generator in a series of field experiments. The sampling method and analysis method used for samples taken in these experiments is investigated in this report. These field measurements were made on a grid of samplers extending out several kilometers downwind from the smoke source.

The smoke generator we have used in these experiments was either a M3A3E3 Smoke Generator, used in the 1985 Dugway Proving Ground Tests, an M3A3 Smoke Generator used at Camp Atterbury in 1986, or a M3A4 Smoke Generator used in 1987 at both Camp Atterbury and in California as a part of project WIND. These generators, which are versions of the same basic machine, are used by the U.S. Army for creating dense smoke clouds to conceal troops. The generator consists of an oil pump and a small gasoline powered ram jet engine. Oil is injected into the jet engine exhaust manifold at a rate of 95 to 227 liters per hour. It vaporizes in the engine and condenses to a heavy fog when it is blown out of the exhaust into the atmosphere.

The oil used in the generators is similar in properties to 10W oil. The distillation temperature of the fog oil ranges from $200^\circ C$ at 10% distillation to 320°C at 90% distillation by volume. It consists of several thousand individual constituents. The properties and chemical composition of the oil did not appear to change significantly through the generation process in our laboratory and field tests, although our analytical method does not allow the resolution of the fog oil into its individual constituents. Such resolution if it is accomplished, may determine the degree to which single species in the fog oil are formed or destroyed in the smoke generating process.

1.3 Sampling Method

In this series of field experiments we have used two basic sampling methods. Dosage Tubes packed with 60/80 mesh Tenax GC were used for collection of the fog oil, both vapor and liquid phases. at

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Dugway Proving Ground in 1985. This method did not prove to be satisfactory, due to contamination of the samplers, and in all the later field studies glass fiber filters were used for sampling the aerosol fraction of the oil at most locations, with only limited use of the Tenax samplers for measuring the vapor fraction of the oil smoke. After aspiration, both the adsorbent tubes and filters were directly analyzed. Cascade impactors were used for measuring the size distribution of the fog oil smoke. The stages of the impactor were wiped with clean glass fiber filters, and the filters were analyzed.

1.4 Analysis Procedure

The analysis of collected sample is accomplished using a high temperature thermal desorption procedure followed by gas chromatography for chemical characterization and quantification of the collected oil. The sample is placed in a modified gas chromatograph injector body and purged of air. It is then heated to vaporize the oil. The carrier gas is switched to flow through the sample tube and the vaporized sample is swept from the tube through a 1:1 flow splitter which allows high flow rates through the sample tube and an optimum flow through the column. Half of the desorbed sample is carried onto a 1.5 m column packed with 3% Dexsil 300, a silicone oil, on 80/100 mesh Chromasorb W HP, a support prepared from diatomaceous silica.

After the oil has been completely swept from the sample tube, the carrier flow is again diverted around the injector. The column oven temperature is simultaneously raised during sample desorption to elute the oil sample from the column. The sample constituents emerge from the column in order of increasing boiling point because of the nature of the column-sample interaction.

A flame ionization detector, which has a selective response to organic compounds, measures the mass concentration of eluting sample. The electrical output from the detector is recorded by an electronic integrator which processes the signal for a total mass measurement. Similar methods sometimes use a cooled precolumn or trap to condense the sample in a narrow band at the beginning of the column. Omitting this trap saves time in the analysis and eliminates problems of condensing and revaporizing the relatively nonvolatile fog oil.

Complete resolution of the constituents in the oil is almost impossible because of the extremely large number of components in the fog oil. It would be impractical to analyze the many thousands of samples we have collected using a high resolution capillary column method because of the time required for each analysis. The method described here gives a good representation of the oil sample. Total collected mass can be found from the data. Fractions of oil components within a given molecular weight range can also be determined.

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2.0 LITERATURE REVIEW

2.1. Oil Fog

The use of oil fog as an atmospheric marker is limited to distances close to the source. It is useful in studies of plume dispersion and ground-atmosphere interaction because of its photogenic properties. The plume emitted from an oil fog generator is a very thick white smoke. The visibility makes the plume very easy to characterize in terms of shape and spreading. The chemical nature of the smoke is not unique. There are many ambient hydrocarbons which could interfere in the chemical analysis if present in high enough concentrations.

Several methods are appropriate for analysis of oil fog. Thse include methods based on the fluorescent property of the oil such as used by Ray (1970), Houghton and Lee (1960), and in NIOSH Method P&ACM 159 (1977). Barad and Shorr (1954) describe a variation of this type of method in an atmospheric disersion experiment using fog oil. Chemical changes in the oil, which may occur during the generation process, cannot be determined with this method, and interferences are possible from other fluorescent material in the atmosphere.

A more chemically selective method for collecting organic vapor samples uses activated charcoal filled adsorbant tubes. After exposure, the organic material is extracted from the charcoal with carbon disulfide and analyzed by gas chromatography. This method was used by Fraust and Hermann (1966), Reid and Halpin (1968), and White et al. (1970) for sampling organic vapors. It is described in NIOSH method P&CAM 127 (1977). It has a sensitivity of $10\mu g$ to $100\mu g$ of sample for many types of organic compounds. Jenkins et al. (1982, 1983) has successfully used a variation of the carbon disulfide extraction procedure for analyzing diesel fuel smoke collected on both filters for the aerosol and using adsorbant tubes for the vapor collection. This method employed a capillary column sufficient for separating the oil sample into its individual chemical constituents. This analysis method will aid in determining the chemical composition of the oil, but is unsuitable for analyzing a large number of samplers because of the sample preparation and analysis time required.

An improved method for analysis of fog oil samples of both aerosol and vapor from field dispersion experiments is described in this paper. The intent of this method is to maintain the accuracy and sensitivity of the previously mentioned procedures while reducing the analysis time and the time required for manual preparation of the samples before analysis. In this method, fog oil is thermally vaporized from a collected sample, swept onto an analysis column, and analyzed by gas chromatography. This allows the gross chemical composition of the sample to be determined. Both glass fiber filters for collecting the aerosol, and absorbant filled tubes for collection of vapor may be used with this method.

2.2 Chromatography

Chromatography is a separation procedure involving the differential migration of sample components carried through an absorptive material. Varying retention affinity of the adsorbent for different components of the sample allows separation of the sample into its chemical constituents. It is practically the only method available for separating different compounds in a multicomponent sample. All chromatography systems employ a separatory adsorbent, a driving force to move the sample through the adsorbent, and a detection method. A good development of the history and theory of chromatography is given by Heftman (1967).

2.2.1. Concepts of Gas Chromatography

A typical chromatogram is shown in figure 2.1. The elapsed time from injection to peak elution is the retention time, t_1. A peak which is unretained by the column travels at the velocity of the carrier gas and elutes from the column in time t_u, which is equal to L/v. L is the column length and v is the velocity of

carrier through the column. The integrated area under a peak is proportional to the amount of the component in the injected sample.

The standard deviation σ, of a peak as a measure of the spread of the sample zone can be found from the chromatogram. The value 2σ is equal to the peak width at 0.607 of the peak height. This is valid if the peak is approximately Gaussian in shape.

An accepted way to present the resolution of the column is given by :

$$N = \left[\frac{t_1}{\sigma_1} \right]^2 \qquad (2.1)$$

The dimensionless number N is called the plate number of the column. It is related to the column length by the plate height H, given by :

$$H = \frac{L}{N} \qquad (2.2)$$

The plate height has units of length. The plate number and plate height vary for different components on the same column. The resolution of two components on a column is determined by both their retention times and the spreading of the zones. The resolution is defined as

$$R_s = \frac{(t_2 - t_1)}{2(\sigma_2 + \sigma_1)} \qquad (2.3)$$

The values of σ and t are the standard deviation and retention time respectively for each of two components. R_s should be greater than one for complete component separation.

2.2.2 Theory of Chromatography

In a chromatograph column, zones of separated material move down the column at some fractional velocity, R, of the carrier, or mobile phase velocity. On a kinetic basis, each molecule alternately moves at the carrier velocity or is temporarily stopped at the stationary phase. Each molecule moves in a random fashion down the column and is stopped for an average time, t_s, or is moving with the carrier for an average time t_m. The zone spreads as it moves down the column due to fluctuations about the average times t_s and t_m by individual molecules. The fractional velocity ratio of the zone to the carrier velocity is:

$$R = \frac{t_m}{(t_s + t_m)} \qquad (2.4)$$

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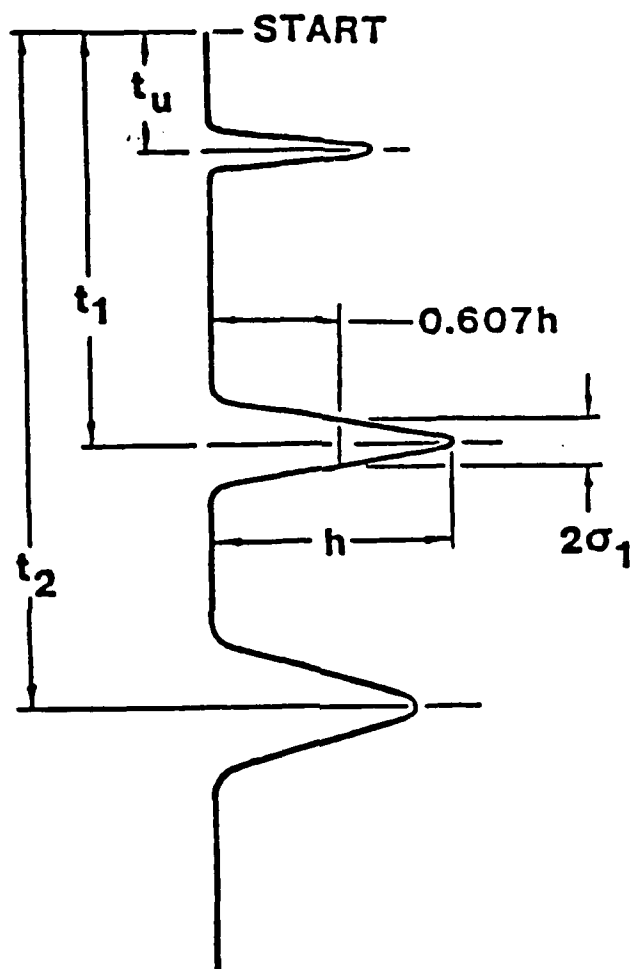
Figure 2.1 Typical Chromatogram and Notation

The phenomena can also be looked at on an equilibrium basis. In a small section of the column, the quantity of sample in the mobile state is the local concentration c_m times the volume of mobile phase, V_m. In the stationary phase, the amount of sample is likewise, $c_s V_s$. The fractional velocity ratio can be expressed in terms of these parameters by :

$$R = \frac{c_m V_m}{(c_m V_m + c_s V_s)} \qquad (2.5a)$$

or

$$R = \frac{V_m}{(V_m + K V_s)} \qquad (2.5b)$$

where

$$K = \frac{c_s}{c_m} \qquad (2.6)$$

The value K is a distribution coefficient or equilibrium constant between the two phases. This is an intensive property of the system. If the mobile phase is a gas, this can also be represented using the partial pressure of the sample in the mobile phase, p_m, by

$$K = \frac{c_s}{k p_m} \qquad (2.7)$$

The value K is a proportionality constant between concentration and pressure in the mobile phase.

The equilibrium constant K, and thus the fractional velocity R, depend on the sample and stationary phase properties and upon the pressure and temperature of the system. The value of K is strongly influenced by the chemical nature of the mobile and stationary phases. Polar phases are usually used for analysis of polar materials and nonpolar phases are used for nonpolar samples. Pressure does not have a great effect on K at the levels found in gas chromatography, or at atmospheric pressure. Temperature has a much greater effect. An increase in temperature increases the amount of sample in the mobile phase and therefore increases the fractional velocity of the zone. Zone spreading occurs due to three physical processes: ordinary diffusion, eddy diffusion, and local nonequilibrium. Ordinary diffusion occurs as sample moves from the central zone of high concentration to the adjacent area of lower concentration. Eddy diffusion is due to the nonuniform flow fields within the column and through the particulates packed in the column. Local nonequilibrium is caused by the finite time required for transfer of sample between phases while the mobile sample fraction continues to move down the column.

One of the simplest but effective models of zone spreading is the random walk model as given by Heftman (1967). In this analysis, the contributions of ordinary diffusion, eddy diffusion, and local nonequilibrium are assumed to be independent. Therefore the standard deviation of the total contribution can be obtained by summation;

$$\sigma^2 = \sum \sigma_j^2 \qquad (2.8)$$

For ordinary diffusion, σ_d is given by

$$\sigma_d^2 = 2\,D\,t \qquad (2.9a)$$

where D is the coefficient of diffusion in the mobile phase and t is the time since the beginning of the process. The time t is also given by L/v, where L is the column length and v is the mobile phase velocity. This gives :

$$\sigma_d^2 = \frac{2DL}{v} \qquad (2.9b)$$

The standard deviation for eddy diffusion and local nonequilibrium are found from random walk theory. Each step in a random walk model is the same length, but the direction is random. If the walk is repeated many times, a plot of number concentration versus distance would give a Gaussian distribution. The standard deviation from random walk theory is

$$\sigma = l\,\sqrt{n} \qquad (2.10)$$

where l is the length of step and n is the number of steps taken.

Eddy diffusion is due to the uneven path lengths and velocities within a column. Each step length is approximately d_p, the diameter of particle packing the column. The number of steps, n, is approximately L/d_p. Substituting into equation 2.10, we get

$$\sigma_e = \sqrt{L\,d_p} \qquad (2.11)$$

Similarly, for local nonequilibrium, the number of steps is the number of transfers between phases, or twice the total number of desorptions. The number of desorptions is the amount of time that a molecule is absorbed divided by the desorption time, t_s. The time required for a zone to move through a column of length L is L/Rv. The time spent in the stationary phase is (1-R)L/Rv. The number of desorptions is this time divided by t_s. The number of steps is then

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$$n = \frac{2(1 - R)L}{Rvt_s}$$
(2.12)

The length of step is the difference of distance traveled by the zone and a molecule in the stationary phase with no velocity in the time interval t_s. This is

$$l = Rvt_s$$
(2.13)

Substituting into equation 2.10, we get

$$\sigma_n = \sqrt{(1 - R) R2vLt_s}$$
(2.14)

Summing the standard deviations from equations 2.9, 2.11, and 2.12, and assuming their independence, gives

$$\sigma_l^2 = \sigma_d^2 + \sigma_e^2 + \sigma_n^2$$
(2.8)

or

$$\sigma_l = L\left[\frac{2D}{v} + d_p + 2R(1 - R)vt_s\right]$$
(2.15)

The standard deviation σ_l represents the concentration of component versus distance. For gas chromatography, a plot of concentration versus time is recorded. The standard deviation in time, σ_t, is

$$\sigma_t = \frac{\sigma_l}{Rv}$$
(2.16)

where Rv is the zone velocity. This gives

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$$\sigma_t^2 = \left[\frac{t^2}{LR^2}\right] \left\{ \frac{2D}{v} + d_p + 2R(1-R)vt_s \right\} \qquad (2.17)$$

Since from equation 2.4 and 2.5,

$$R = \frac{V_l}{v} = \frac{t}{t_1} \qquad (2.18)$$

where v is the carrier velocity, V_1 is the velocity of zone 1, t is the time required for carrier gas to move through the column, and t_1 is the time required for zone 1 to elute from the column, we can substitute equation 2.18 into equation 2.17 and get

$$\sigma_{t_1} = \left[\frac{t_1^2}{L}\right] \left\{ \frac{2D}{v} + d_p + 2R(R-1)vt_s \right\} \qquad (2.19)$$

From the definition of plate number in equation 2.1 and from equation 2.19 we get

$$N = \frac{L}{\left\{ \frac{2D}{v} + d_p + 2R(1-R)vt_s \right\}} \qquad (2.20)$$

The plate height from equation 2.2 is given by

$$H = \frac{2D}{v} + d_p + 2R(1-R)vt_s \qquad (2.21)$$

This could also be found from the definition of the plate height using the standard deviation in space,

$$H = \frac{\sigma_l^2}{L} \qquad (2.22)$$

Increasing the resolution of a column may be accomplished by reducing the plate height. From inspection of equation 2.21, an increase in carrier velocity decreases the first term but increases the last term. This suggests that an optimum carrier velocity may be found for

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$$\frac{dH}{dv} = -\frac{2D}{v^2} + 2R(1 - R)t_d = 0 \qquad (2.23)$$

Solving for v, the optimum velocity for highest resolution of a component on a column is

$$v = \sqrt{\frac{D}{R(1 - R)t_d}} \qquad (2.24)$$

In actual practice the resolution is not very sensitive to carrier velocity near the optimum and a higher velocity may be used to speed up the analysis. A smaller diffusion coefficient would also increase the resolution. This implies that a heavier gas would produce better component separation. A liquid carrier, as used in liquid chromatography would also increase the resolution for the same reason. The theory assumes that the diffusion of sample to the surface of the adsorbent occurs much faster than the flow of sample through the column. This assumption does not always hold, especially for very high carrier flow rates.

Smaller particles in the column would increase the resolution by decreasing d_p in equation 2.21. This also decreases t_s because of coupling effects which were neglected in this analysis. Open bore columns or capillary columns eliminate the particles altogether and have much better resolution than packed columns but at the expense of decreasing the sample size and increasing the analysis time.

2.3 Gas Chromatography

A schematic representation of a chromatograph is given in figure 2.2. Carrier gas flows through a controller and regulator, then through the injection port, through the column, which is contained in a temperature regulated oven, and on to a detector. which supplies an electrical output to a recorder or logging device.

2.3.1 Carrier Gas

The carrier gas may be any pure gas such as nitrogen or helium. The selection of a gas most often depends on the detector used. The flow rate of the carrier is precisely regulated, first by a two stage regulator on the gas cylinder and then by a pressure regulator or by a mass flow controller. For chromatographs operated with varying oven temperatures, a mass flow controller is required because the resistance of the column to flow varies widely with temperature. The flow rate is usually measured with a rotameter or a bubble flow meter. Purity of the carrier gas is important because some contaminants may cause degradation of the column or high detector noise levels.

2.3.2 Sample Introduction

Samples are usually introduced into a chromatograph through a heated injector port. A cutaway diagram of an injector body is shown in figure 2.3. Carrier gas flows up the outer concentric tube and back through the center tube to the column. The injector is maintained at a temperature high enough to vaporize the sample. A sample is introduced by inserting a syringe needle through the septum into the center tube. The injected sample quickly vaporizes and is carried onto the column. Other methods used to introduce samples such as those collected on adsorbent or cryogenic traps will be covered on the section on thermal desorption.
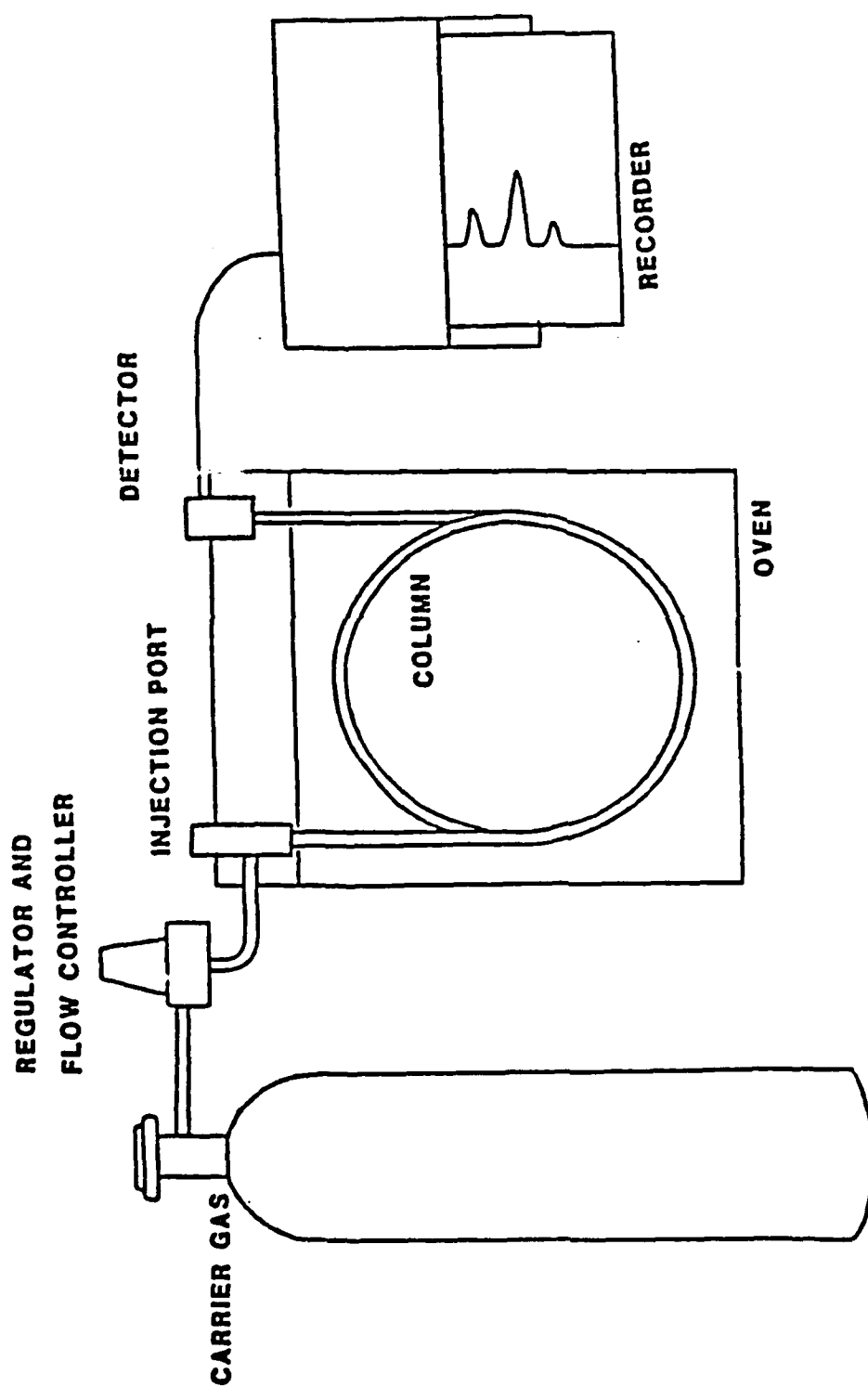
Figure 2.2 Schematic of a Gas Chromatograph

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HEATED AREA

OUTER CONCENTRIC TUBE

INNER CONCENTRIC TUBE

CARRIER GAS INLET

CARRIER GAS PATH INDICATED BY ARROWS

TO COLUMN

SEPTUM

SEPTUM CAP
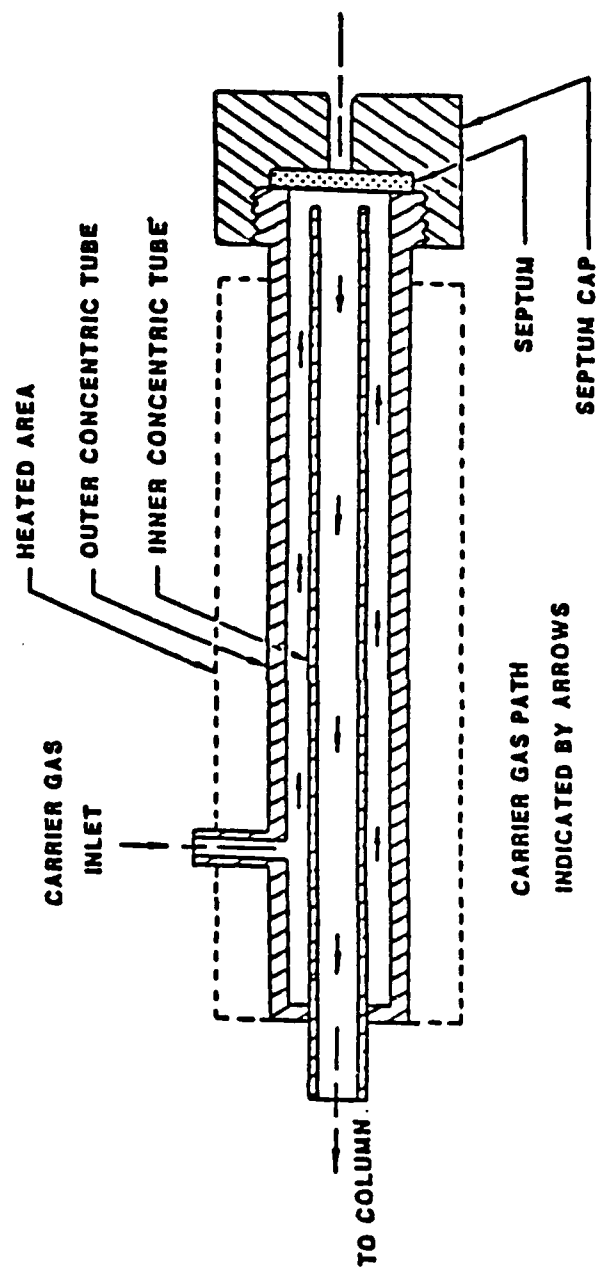
Figure 2.3 Gas Chromatograph Sample Injector Schematic

2.3.3 Columns

The chromatograph column oven temperature must be precisely controlled for repeatable results. Retention of compounds on the column is a strong function of temperature. For samples with constituents that have a wide boiling point range, usually about 100°C, most chromatographs have a provision for linearly raising the oven temperature automatically during an analysis. This speeds up the process and provides better resolution of eluting peaks.

Columns may be classified into packed types or capillary types. Capillary columns generally have better resolution and are more sensitive to overloading and contamination than packed columns. They will not be discussed in this paper. Packed columns may be either packed with a particulate solid adsorbent which is called gas-solid chromatography or with inert particles coated with a liquid phase which is gas-liquid chromatography. The chemical nature of the solid packings and liquid phases range from polar to nonpolar and they are selected on the basis of the compounds to be separated.For trace analysis, one-eighth inch diameter columns are generally used.

2.3.4 Detectors

Gas chromatograph detectors provide a way of quantifying the sample components eluting from a column. There are many types of detectors available depending on the application. A flame ionization detector (FID) will detect organic components. Many types of detectors including the FID are described by David (1977).

The FID consists of an air-hydrogen flame in which the column effluent is burned. Such a flame normally has a very low concentration of ions. When an organic compound elutes from the column, a tremendous increase in ion concentration occurs in the flame. Collection of these ions is accomplished by a pair of electrodes held at a high voltage in close proximity to the flame.

The detector output from an FID is proportional to the number of carbon atoms in the flame for many types of organic compounds. This corresponds to a mass concentration response. The exact nature of ion generation in an FID is unknown. According to a compilation of studies by David (19/7), the extent of ionization is not sufficiently accounted for by thermal ionization, but is more likely due to chemi-ionization.

Simple detectors like the FID provide qualitative identification of compounds by comparison of retention times for known reference compounds with that of the unknown sample. This is adequate when a known reference can be obtained. For identification of specific compounds when a reference is not available, a gas chromatograph - mass spectrometer combination is used. The mass spectrometer is coupled to the column effluent.

2.4 Gas Chromatography of Hydrocarbons

Any petroleum fraction is composed of many thousands of individual constituents. For example, several hundred constituents have been identified in fog oil by Katz et al. (1980). Many more peaks were unidentified or unresolved. The analysis consisted of class fractionalization of the sample by liquid chromatography followed by gas capillary chromatography with mass spectrometry. It has also been used for diesel fuel by Jenkins et al. (1982). The entire analysis is both laborious and time consuming, but yields detailed information on the chemical composition of the oil.

Another method for chromatographic analysis of oil is ASTM method 2887 for petroleum fractions and ASTM method 3710 for gasoline fractions. The basic method is also described by Adlard in Heftman (1983).These methods provide for separation of oil components by increasing boiling point or molecular weight. While complete resolution of the oil is not obtained, a chromatogram of the oil is produced which

can be used to find a distillation curve for the oil, or mass fractions of the sample within a certain molecular weight range.

In this method a short packed column with a non-polar silicone oil as the stationary phase is used. Upon introduction of the sample, the column temperature is ramped to elute the oil. A run consisting of n-paraffins under similar operating conditions is used to correlate boiling point with retention time. A typical chromatogram of fog oil produced using this method is given in figure 2.4.a. An analysis of a series of n-paraffins is shown in figure 2.4.b. From the chromatogram of the n-paraffins, a linear relationship between elution time and boiling point is found, as illustrated in figure 2.5. This allows a temperature axis to replace the time axis of the chromatogram so that information on the distillation temperature range and molecular weight composition of the oil may be found.

2.5 Sample Collection Methods

2.5.1 Sampling of Gases and Vapors

Many methods have been used for collection of atmospheric samples. Gases and vapors have been collected using either whole air samples or concentration techniques.

2.5.1.1 Whole Air Sampling

Whole air samples may be taken using plastic bags with pumps, syringes, plastic squeeze bottles, or evacuated bottles. Sensitive detection techniques are needed for whole air sampling, such as gas chromatography - mass spectrometry as used by Grimsrud and Rasmussen (1975) for background measurements, or an easily detectable tracer such as sulfur hexaflouride as used by Collins, et al. (1965), Saltzman et al. (1966), Drivas and Shair (1974), and Niemeyer and McCormick (1974).

2.5.1.2 Cyrogenic Sampling

Cryogenic sampling has been used for preconcentration of gases to provide better detection capability. An adsorbent trap is usually immersed in the coolant and aspirated to collect the gases. Liquid nitrogen samplers have been used for collection of ambient and heavy methane by Cowan et al. (1976) and Dietz and Dabberdt (1983) as well as for collection of atmospheric pollutants by Bellar et al. (1963). Collection traps at dry ice - acetone temperatures were used by Brenner and Ettre (1959) for collection of trace impurities from large samples, by Altshuller et al. (1962) for collection of hydrocarbons, and by Ludwick (1966) and Eggleton and Thompson (1961) for collection of radioactive xenon tracer.

2.5.1.3 Adsorbent Samplers

Adsorbent samplers are used at ambient temperature for collection of less volatile vapors. These usually consist of short sections of tubing packed with a suitable particulate adsorbent.

Silica gel has been use in adsorbent samplers by Whitman and Johnston (1964) for sampling of hydrocarbons in air. The sample was extracted from the silica gel using isopropylbenzene and water. An aliquot of the extract was then analyzed in a gas chromatograph. Cropper and Kaminsky (1963) also used silica gel in atmospheric sampling, but the collected sample was thermally desorbed from the sampler.

Silica gel is a polar adsorbent and preferentially absorbs polar compounds, such as water vapor. According to Cropper and Kaminsky, the preferential absorption of water may displace some compounds of interest. In addition water has an adverse effect on the response of some gas chromatographic detectors, including the electron capture detector.

Activated charcoal, which is a non-polar adsorbent and does not absorb water vapor has been used by Cropper and Kaminsky (1963), and Murray and Riley (1973) for sampling organic vapors for later

22
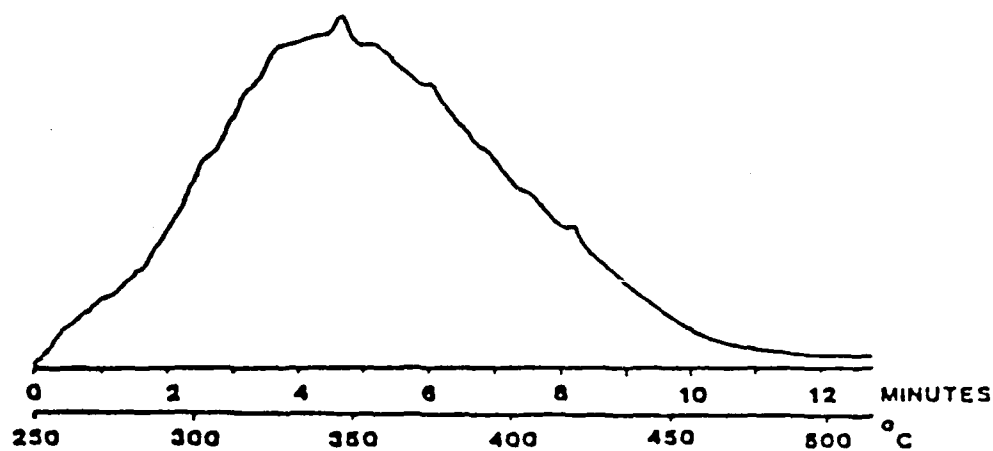
a) Fog Oil Sample
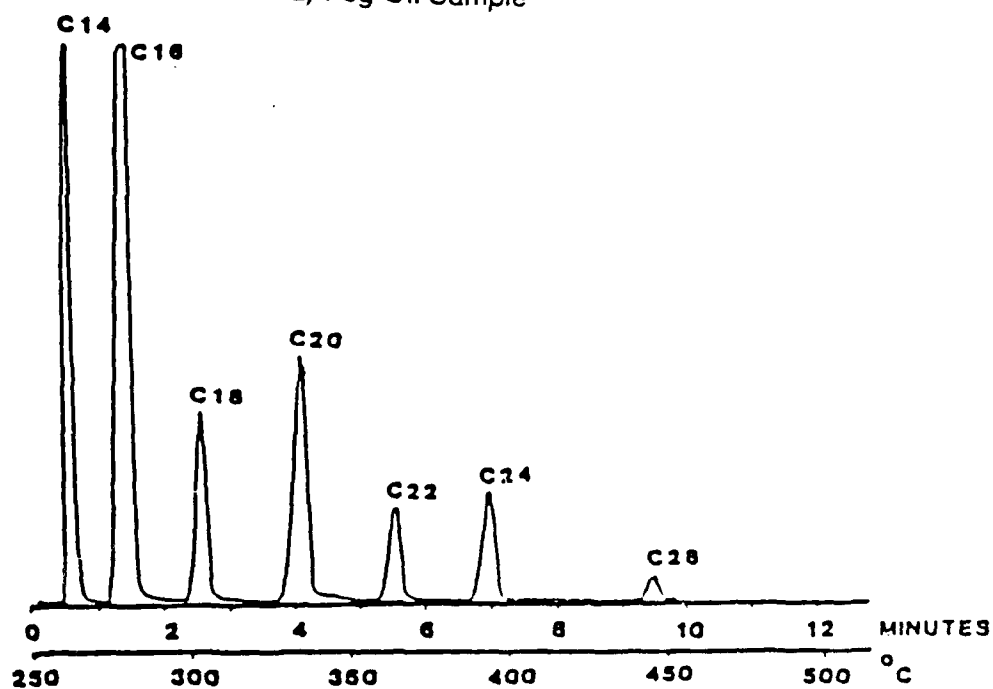
b) Sample of a n-Paraffin Mixture

Figure 2.4 Chromatograms of Hydrocarbons Produced with
a Separation by Increasing Boiling Point Method

23
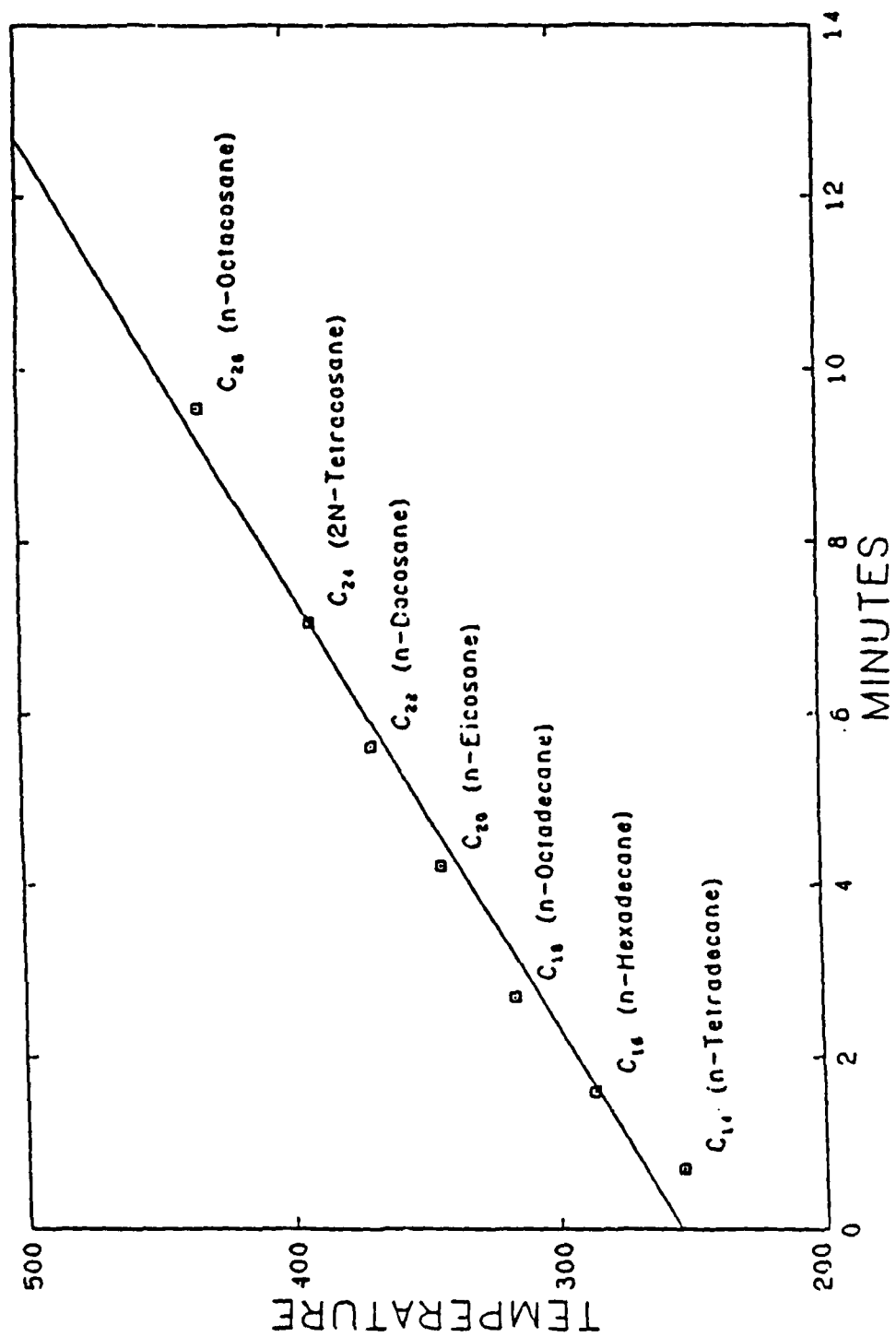
Figure 2.5 Elution Time versus Component Boiling Point
for n-Paraffin Analysis

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thermal desorption in sample analysis. It has also been used by Fraust and Hermann (1966), Reid and Halpin (1968), and White, et al. (1970) where the sampler was exposed and the organic material then extracted with carbon disulfide for analysis by gas chromatography. This method of extraction is described in NIOSH method P&CAM 127 (1977).

Some types of compounds have been found to be permanently absorbed on activated charcoal or have low desorption efficiencies. This is due to the presence of very active absorption sites on the charcoal which may cause strong chemical bonding of sample molecules to the adsorbent.

Some types of porous polymers have also been used as adsorbents. They are commercially available under various trade names. The porous polymers used as adsorbents are non-catalytic and reduce the possibility of sample decomposition. Porapak-N was used by Russell and Shadoff (1977) for collection of halocarbons and gas chromatographic analysis with an electron capture detector. They reported problems with water vapor collected on the adsorbent. Gelbicova-Ruzickova et al. (1972) reported on the use of Porapak P and Q, which are both hydrophobic, in the determination of halothane concentrations using a flame ionization detector.

Comparison of several types of adsorbents and porous polymers were reported by Russell (1975).Tenax-GC, Porapak N, Porapak R, and silicone oil on a solid support were exposed to a sampling of organic pollutants. Breakthrough volume, which is the amount of air that can be drawn through a sampler before components begin to pass through the sampler are reported. Tenax-GC was found to have the highest breakthrough volume of the tested adsorbents, and a very low affinity for water. In addition to total volume sampled, it was found that the flow rate through the sampler was also critical. If the air velocity through the sampler was too high, an insufficient time of contact between pollutant and adsorbent resulted, with some pollutant passing through the tube without being absorbed. The actual maximum flow rate depends on the adsorbent and the sampled compound.

Tenax-GC has also been used to collect the volatile fraction of of a diesel fuel aerosol as reported by Jenkins et al. (1982) with analysis by thermal desorption. It has been similarly used by Bertsch et al. (1974) for atmospheric sampling in which organic components from C_5 to C_{16} are recognizable. Because of its hydrophobic nature, it has also been used to concentrate volatile compounds from aqueous solutions in headspace analysis as reported by Zlatkis et al. (1973).

2.5.1.4 Modeling of Adsorbent Samplers

The collection efficiency of adsorbent samplers for various vapors in the air needs to be found before the vapor can be quantitatively collected. If the sample tube is thought of as a chromatographic column, when the tube is aspirated collected vapor will pass through the tube at some fraction of the air velocity through the tube. Various types of vapors will move at different fractional velocities. As the sample moves through the tube, there is a critical aspirated volume when the front of the sample band begins to pass off the sample tube. This is called the breakthrough volume, V_b. It is defined by Senum (1981) as the sampled volume when a given fraction of sample has passed through the tube, compared to that which has been collected on the tube.

An adsorbent sampling tube can be modeled as a short chromatographic column for determination of breakthrough volume. The response of a column to various input profiles is discussed by Reilley et al. (1962). The response for an impulse and a step input are shown in figure 2.6. The response to a step input in ambient concentration as a function of time has been determined to be

$$R(t) = \frac{C}{2} \left[\text{erfc} \left[\frac{(t_r - t)}{\sigma \sqrt{2}} \right] + \text{erfc} \left[\frac{t_r + t)}{\sigma \sqrt{2}} \right] \right] \quad (2.25)$$

25
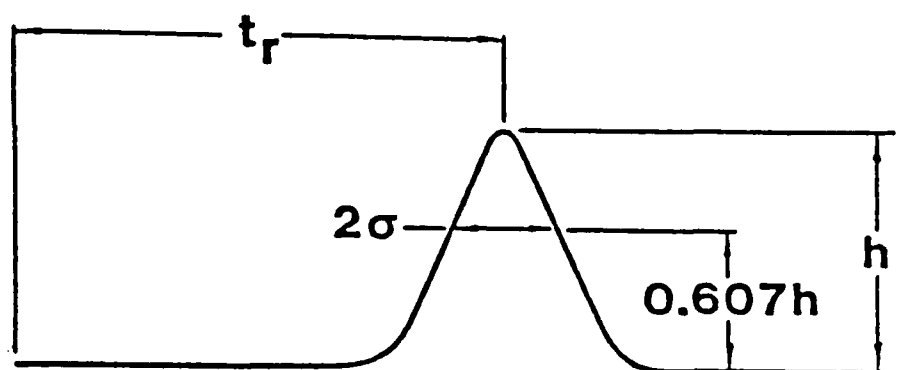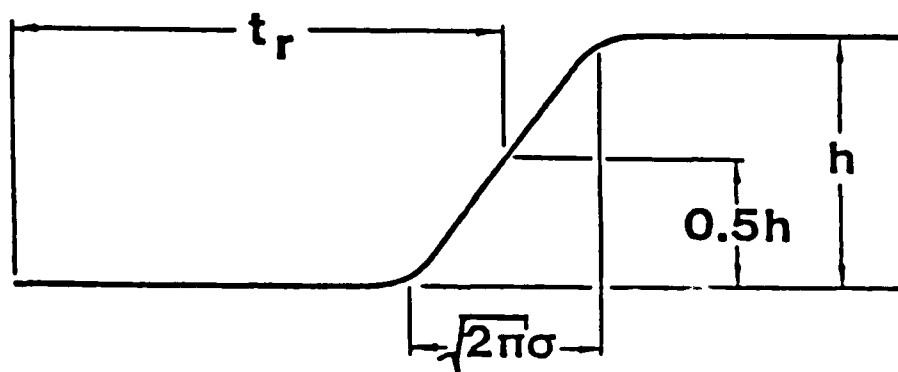
a) Impulse Input

b) Step Input

Figure 2.6 Column Response for Different Input Profiles

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The value t_r is the time required for R to reach half the value of C. It also corresponds to the retention time for an impulse input. Introducing into equation 2.25 the plate number, N, the retention volume V_r, which is the sampled volume in time t_r, and the sampled volume V, which is the volume drawn through the tube in time t, Senum (1981) has found that

$$R(V) = \frac{C}{2}\left[\text{erfc}\left[\left\{ 1 - \frac{V}{V_r} \right\}\sqrt{\frac{N}{2}} \right] + \text{erfc}\left[\left\{ 1 + \frac{V}{V_r} \right\}\sqrt{\frac{N}{2}} \right] \right]$$
(2.26)

A plot of equation 2.26 is given in figure 2.7 for several different plate numbers, N. It can be seen from this plot that the collection efficiency of the sampler is a function of both the sampled volume and the plate number of the sampling tube. Collection efficiency decreases with increasing aspirated volume and increases with increasing plate number.

Defining the breakthrough volume V_b, as the sampled volume when a fraction f, of the sample has passed through the adsorbent,

$$f = \frac{\displaystyle\int_0^{V_b} R(V)\,dV}{\left[CV_b - \displaystyle\int_0^{V_b} R(V)\,dV \right]}$$
(2.27)

Substituting equation 2.26 into equation 2.27 and integrating,

$$\frac{2f\left[\dfrac{V_b}{V_r} \right]\sqrt{\dfrac{N}{2}}}{(1 + f)} = \text{ierfc}\left[\left\{ 1 - \frac{V_b}{V_r} \right\}\sqrt{\frac{N}{2}} \right] - \text{ierfc}\left[\left\{ 1 + \frac{V_b}{V_r} \right\}\sqrt{\frac{N}{2}} \right]$$
(2.28)

The function ierfc(x) is the integral of the complementary error function. The collection efficiency as a percentage of the sample which remains on the adsorbent is
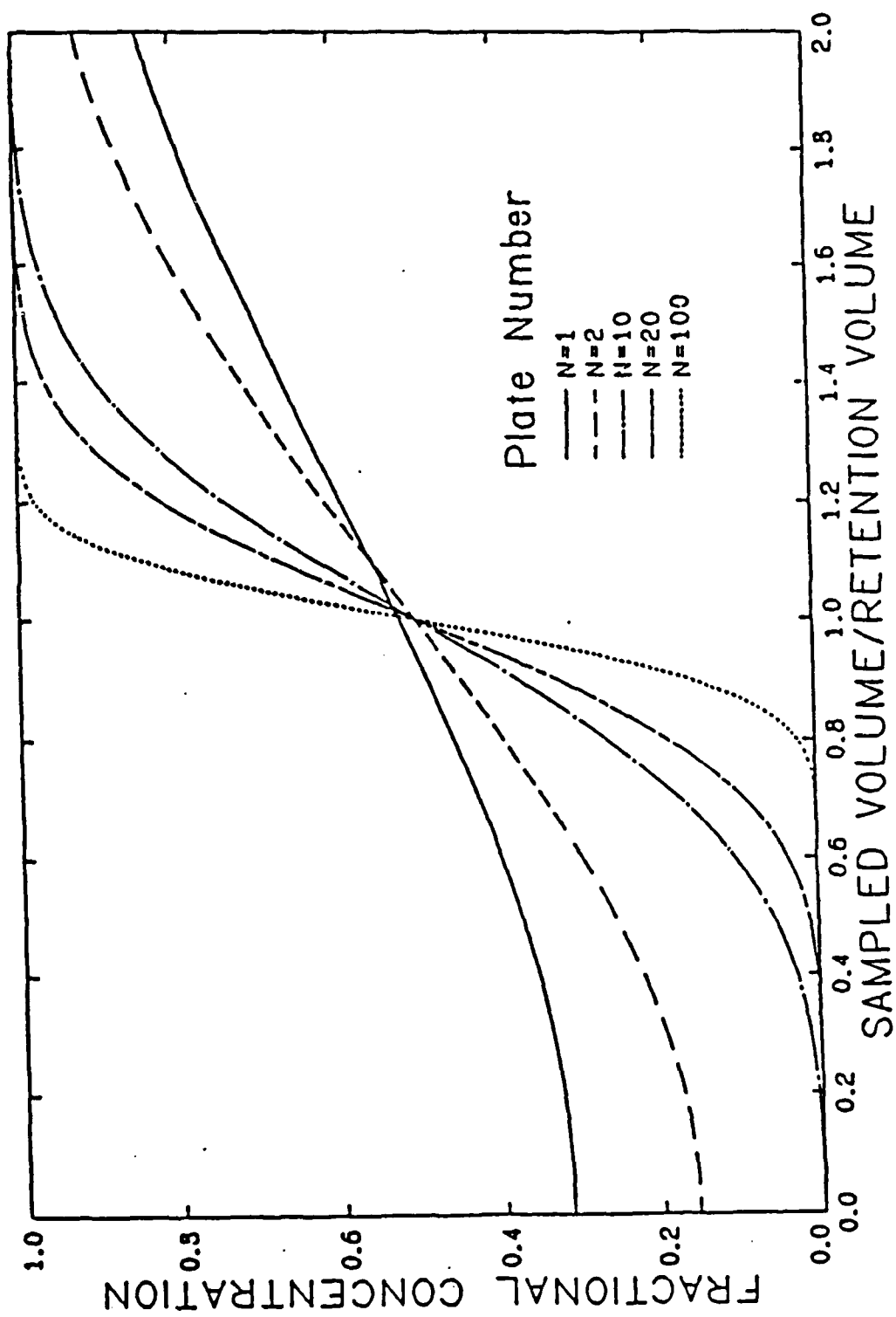
Figure 2.7 Collection Efficiency of an Adsorbent Tube Sampler

$$collection\ efficiency = 100(1 - f) \qquad (2.29)$$

The collection efficiency of a sample tube can be determined by mounting the tube in a gas chromatograph between the detector and injection port, injecting sample onto the port, and monitoring the detector output. Efficiency may also be checked by aspirating sample vapor through a series of two sample tubes. The backup tube is replaced at intervals of time and analyzed to determine the aspirated volume when sample breaks through the front sample tube.

All of the factors affecting plate number and retention time of a chromatographic column as discussed in section 2.2 have the same effect on a sampling tube. Deviations from linearity may adversely affect the collection efficiency. Nonlinearity of sampler response may arise from unequal absorption - desorption effects and multidimensional effects which were neglected in the analysis of section 2.2. At higher sampler loading, saturation of absorption sites may cause lower collection efficiency. It is also useful to note that as the plate number N varies with flow rate, sampler efficiency is also a function of flow rate. Multiple components may also alter collection characteristics as various compounds compete for absorption sites.

2.6 Thermal Desorption

Thermal Desorption is a method of purging collected vapors from adsorbents using chromatographic equilibration. The sample tube, packed with adsorbent, is heated and the previously collected vapors are swept onto a chromatographic column for analysis. An ideal adsorbent would have a high affinity for vapors at ambient temperatures and no affinity at elevated temperatures. After desorption the samplers, free from collected vapor, are again ready for exposure. This method is less time consuming and simpler than the collection of vapors using bubblers or liquid extraction methods. It also decreases the chance of errors due to manual sample extraction and preparation.

Russell and Shadoff (1977), Russell (1975), Gelbicova-Ruzickova et al. (1972), Novak (1965), and Cropper and Kaminsky (1963) all describe desorption methods employing external heaters to desorb tubes with the vapor from the tubes being directed through the injection port of a chromatograph and onto a column. Zlatkis et al. (1973) and Bertsch et al. (1974) employ the injector heater for desorbing the sample tubes. The tubes conveniently fit within the body of the injector. This setup is more convenient than the external heater because it permits accurate control of the desorption temperature with existing equipment and minimal modification to the chromatograph. The desorption system we are using is similar to the latter method.

Some of the authors employed cooled traps or precolumns to collect the desorbed sample in a narrow band ahead of the column, then warming the trap when the tube desorption is complete. This improves the resolution of the analyzed sample components, because the minimum peak width for an eluted component from a column cannot be less than the width of the sample as it enters the column. The physical size of a desorption tube limits the minimum sample width, while a smaller cooled trap reconcentrates the sample and overcomes this difficulty.

2.7 Particle Collection

There are many methods for collection of atmospheric aerosols. Filtration, wet impingement, impaction and electrostatic precipitation all may be used for sampling fog oil smoke. Filtration and impaction are methods which we have used for collection of oil fog. These methods are suitable for chemical analysis of the collected material.

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2.7.1 Filtration

Glass fiber filters are the most suitable type of filter for our application because they may be desorbed at high temperatures. They have been widely used for sampling the particulate fraction of cigarette smoke as discussed by Wartman, et al. (1959). The collected material was extracted for chemical analysis with chloroform. This method has also been used by Ray (1970) for sampling oil mists. In this case, the oil was quantified by its fluorescence under ultraviolet radiation.

Particulate samples collected on glass fiber filters have been analyzed for polycyclic aromatic hydrocarbon (PAH) content by extracting the filter with cyclohexane and analyzing the extracted matter using chromatography. Searl, et al. (1970), Lao, et al. (1973) and Bjorseth and Lunde (1977) all describe variations of this method. Bertsch et al. (1974) have analyzed particulates on filters for hydrocarbons by thermal desorption in a method similar to that used for absorption samplers.

Jenkins et al. (1982) describes a system for sampling concentrated smoke. It consists of a glass fiber filter for collection of particulates backed by a Tenax-GC trap for collection of vapors. The Tenax traps were analyzed by thermal desorption, and the filters by chemical extraction. They found for a diesel fuel aerosol, components with a boiling point below that of tridecane (n-$C_{13}H_{28}$) remained vapor, while higher boiling compounds condensed to a liquid aerosol.

The chemical composition of collected matter on a filter may be biased by high flow rates. Katz and Chan (1980) in experiments with PAH sampling, and Jenkins et al. (1982) in sampling of nicotine have indicated that high flow rates may cause stripping or evaporation of relatively nonvolatile components from particulates on a filter. Limiting the maximum flow velocity to about 1 m/min alleviated the problem of nicotine evaporation in the second case.

Filtration efficiency of fiber filters is a function of the particle size, air velocity through the filter, and the geometry of the filter. If a particle is too large to pass between filter fibers, it will be intercepted. For lower flow velocities or smaller particles, diffusion of particles from the airstream to the fiber surface is dominant. At higher flow velocities or with larger particles, inertial forces will cause particles to deviate from the streamlines through the filter and impact on the filter fibers.

2.7.2 Particle Impactors

Inertial impactors selectively collect particles on the basis of aerodynamic diameter. The aerodynamic diameter and the actual particle diameter are the same for a spherical unit density particle. The basic schematic for an impactor is given in figure 2.8. Air is drawn through the nozzle and deflected by the impaction plate. Particles of low inertia are able to follow the streamlines around the collection plate, while particles of higher inertia deviate from the streamlines and impact on the collection plate. The particle trajectory in an impactor depends on the flow field within the impactor and the particle Stoke's number given by

$$St = \frac{C_s D_p^2 \rho_p U_o}{9\mu W} \qquad (2.30)$$

St is the ratio of the particle stopping distance to half the nozzle throat diameter. D_p is the particle diameter, ρ_p is the particle density, U_o is the average velocity through the nozzle throat, μ is the fluid viscosity, and W is the jet width. The Cunningham slip correction factor C_s accounts for the noncontinuous fluid behavior when the particle size is the same order as the mean free path of the fluid.
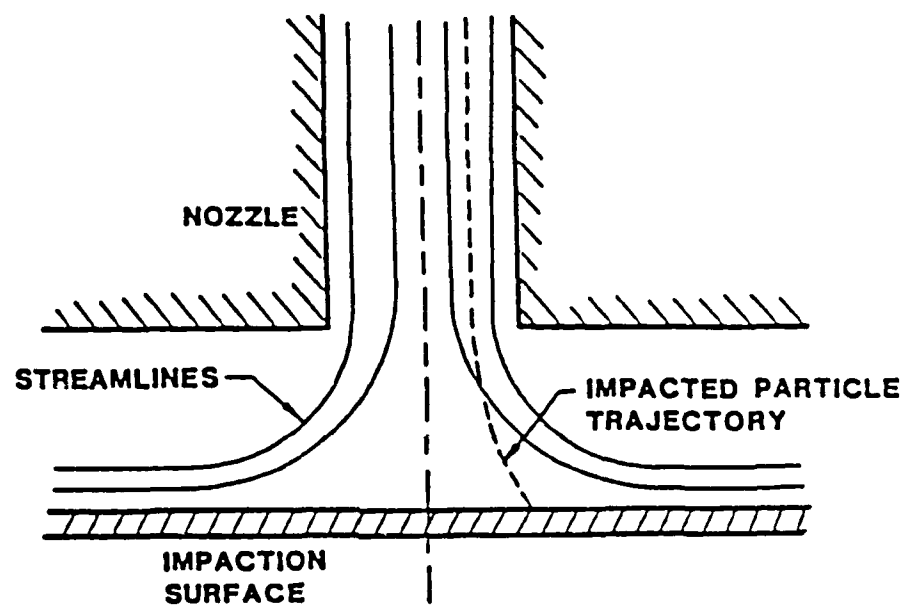
Figure 2.8 Schematic of a Particle Impactor

Ideally, the collection efficiency of an impactor is a function only of Stoke's number. Studies by Cohen and Montan (1967), Marple and Liu (1974), and McFarland and Zeller (1963) have established ranges of jet geometries and flow rates over which changes in the parameter of interest do not significantly affect collection efficiency. Designing and operating an impactor in these ranges reduces sampling errors, makes calibration easier, and improves the measurement accuracy.

For a given impactor, a higher Stoke's number means collection efficiency is higher, and likewise for a lower Stoke's number, collection efficiency is lower. The effective cut diameter is the particle diameter for which the collection efficiency is fifty percent. Aerosol size distribution is better represented by an impactor with sharp cut points. Collection efficiency and effective cut diameter values for a given impactor must be experimentally determined.

Multistage impactors, which have decreasing cut diameters on succeeding stages are used to measure aerosol size distribution. Aerosol collected on a given stage is in a size range between the cut point of the stage and that of the preceding stage. Log-probability graphs of effective cut diameter versus the cumulative mass percentage less than the effective cut diameter are used for data analysis. A straight line on such a plot would indicate a unimodal size distribution of aerosol from which the mass mean particle diameter and geometric standard deviation of the size distribution are found.

To prevent particle from bouncing off the impaction plate, it is usually coated with a thin layer of grease. Particle bounce may cause large deviations in measured versus actual aerosol size distribution. Evaluation of the effect of particle bounce for various impaction substrates is covered by Rao and Whitby (1978). For liquid aerosols such as oil fog, this grease is not necessary because of the adhesion of the liquid droplets to solid surfaces. The grease would also interfere with the chemical analysis of the oil.

2.7.3 Aerosol Sampling Errors

Measurement of particulate concentration and size distribution of an aerosol may be biased by the sampling method. The most prevalent source of errors may to inlet losses or deposition of particles in sampling lines because of particle inertia. Other forces. such as gravity and electrostatic forces do not have a great effect on inlet sampling errors of atmospheric aerosols in the size ra· je of the fog oil smoke.

Deposition of particles in sampling lines may be a problem when an instrument is connected to a source through a long sampling tube. For short inlet sections this problem is negligible. Deposition of particles between stages of a cascade impactor is a problem. For this reason, cascade impactors are not used for total concentration measurements, but only to measure particle size distribution.

Inertial errors may also occur because the sampler inlet is not aligned with the flow direction, or the sampling velocity is not the same as the stream velocity. This problem is called anisokinetic sampling and is covered in papers by Belyaev and Levin (1974), Jayasekera and Davies (1980), Agarwal and Liu (1980), Selden (1977), as well as others.

Various inlet configurations have been used to obtain valid atmospheric aerosol samples. For micron sized particles including oil fog, inertial collection losses have been found to be small. They are significant for larger particles such as road dust and fly ash.

3.0 EXPERIMENTAL APPARATUS

Much of the work associated with this report was involved in implementing an accurate and reliable method for analysis of oil samples by thermal desorption. This section covers the development of a thermal desorption analysis system for oil samples, sampling methods, and construction of a laboratory smoke generator.

3.1 Gas Chromatograph

The gas chromatograph used is a Perkin-Elmer Sigma 300. The instrument is equipped with both a flame ionization detector (FID). Nitrogen carrier gas is used. A heated, flash vaporizing injector for packed 1/8 in and 1/4 in columns is also mounted on the instrument.

The ultra high purity nitrogen carrier gas passes through a two stage regulator, then through a molecular sieve filter to remove traces of water and hydrocarbons. It then passes through a filter packed with an active metal to remove traces of oxygen and another molecular sieve filter before passing to a laminar element flow controller. This flow controller maintains a constant mass flow with changing column back pressure. From the flow controller, the carrier gas may be routed to the injector port or to an apparatus for thermal desorption.

Ultra pure carrier grade hydrogen containing less than 0.5 ppm of hydrocarbons and zero grade air with less than 1 ppm of hydrocarbons are used in the FID. Hydrogen flows through the detector at 60 ml/min and air at 430 ml/min. These flow rates permit high sensitivity with low detector noise.

3.1.1 Data Acquisition and Reduction

The output from the two detectors is handled by a LCI-100 Laboratory Computing Integrator and a 316 Remote Integrator from Perkin-Elmer. Both data acquisition devices are controlled from a Perkin-Elmer 7500 Laboratory Computer over a IEEE-488 parallel interface. Data is acquired by each integrator at 1.56 points/s. A built in algorithm in each integrator provides automated peak detection and integration capability. The data from each integrator is stored on the computer.

Chromatographics 3 software from Perkin-Elmer is used to program and control the integrators, including automated valve switching. The software also provides extensive reintegration and replotting capability for stored chromatograms. Customized programs were added to translate the Perkin-Elmer software output into usable form automatically after each analysis.

3.1.2 Analysis of Oil by Injection

To determine the practicality of analyzing the fog oil by gas chromatography with a packed column, the system was set up for injections of oil using a 1.2 m 3% Dexsil 300 on Chromasorb WHP column. The chromatograph operating conditions are given in table 3.1. Plots of the results for fog oil and for a mixture of n-paraffins are shown in figure 3.1. These results compare favorably with chromatograms of fog oil given by Katz et al. (1980), although they indicate the presence of higher molecular weight hydrocarbons than previously reported. Positive identification of constituents is not possible with the present detector.

The reduced separation of n-paraffins and reduced analysis time from an increased ramp temperature rate are evident from the figure. Injections of n-hexadecane (C_{16}) and n-heptadecane (C_{17}) gave a resolution R_s (equation 2.3), of 0.93 for a ramp rate of 12°C/min and R_s of 0.89 for a ramp rate of 25°C/min. This indicates near complete separation of these two components in both cases. Since the resolution appears relatively insensitive to ramp rate in this range, the higher ramp rate is used because of the decreased analysis time.

Table 3.1 Chromatograph Operating Parameters for Injection Analysis of Fog Oil

Detector:	FID
Column:	1.2 m, 0.22 cm i.d., 0.32 o.d., 3%
	Dexsil 300 GC on Chromasorb WHP
Temperatures	
Injector:	300°C
Detector:	375°C
Column:	
Initial:	150°C
Final:	300°C
Rate:	12°C/min or 25°C/min
Carrier gas:	Nitrogen, Ultrapure
Flow rate:	40 ml/min
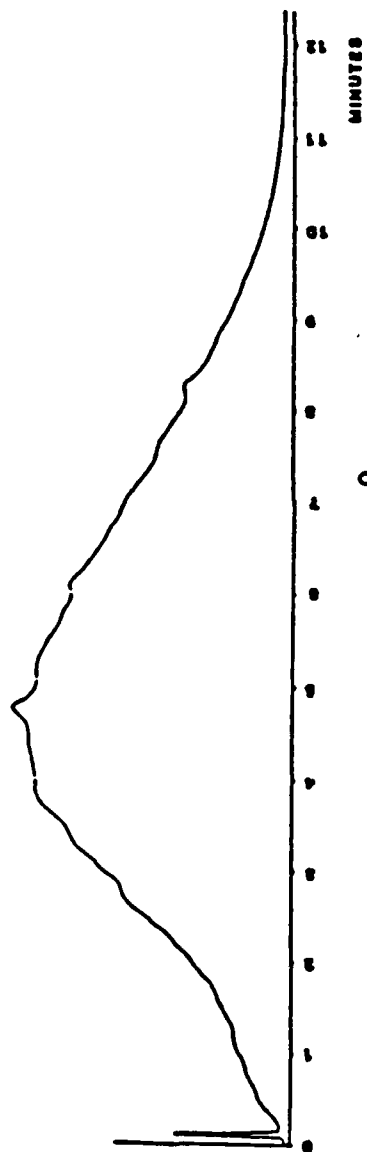
(a) Fog Oil with Oven Rate at 12°C/min

(b) n-Paraffin Mixture with Oven Rate at 12°C/min
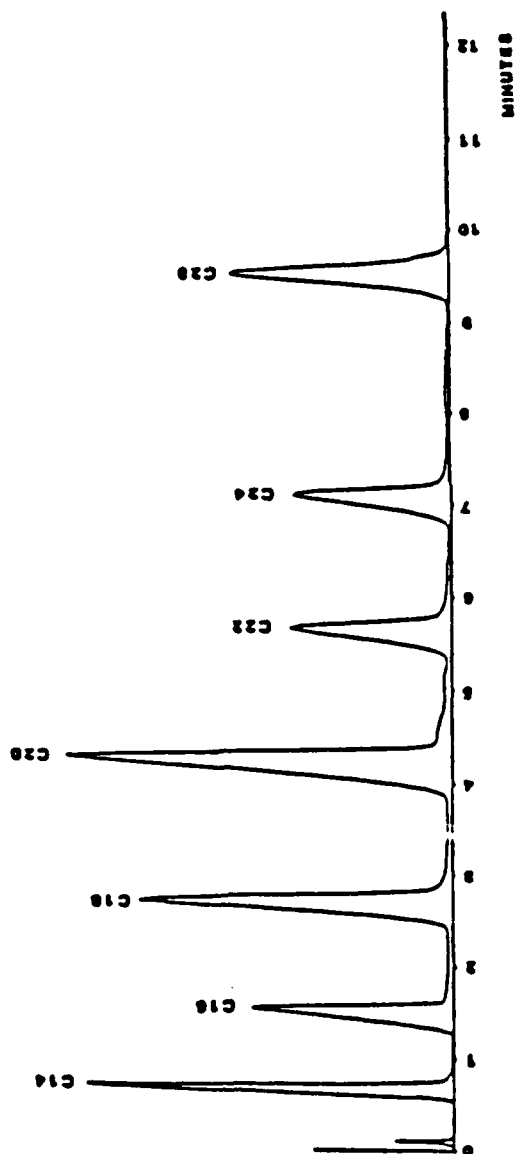
Figure 3.1 Chromatograms of Fog Oil and a n-Paraffin
Mixture for Two Oven Ramp Rates

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(c) Fog Oil with Oven Rate at 25°C/min

(d) n-Paraffin Mixture with Oven Rate at 25°C/min
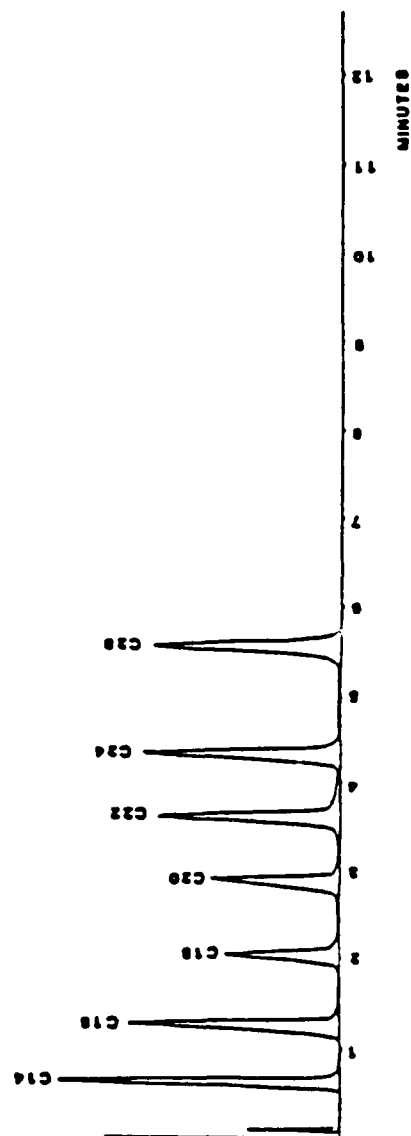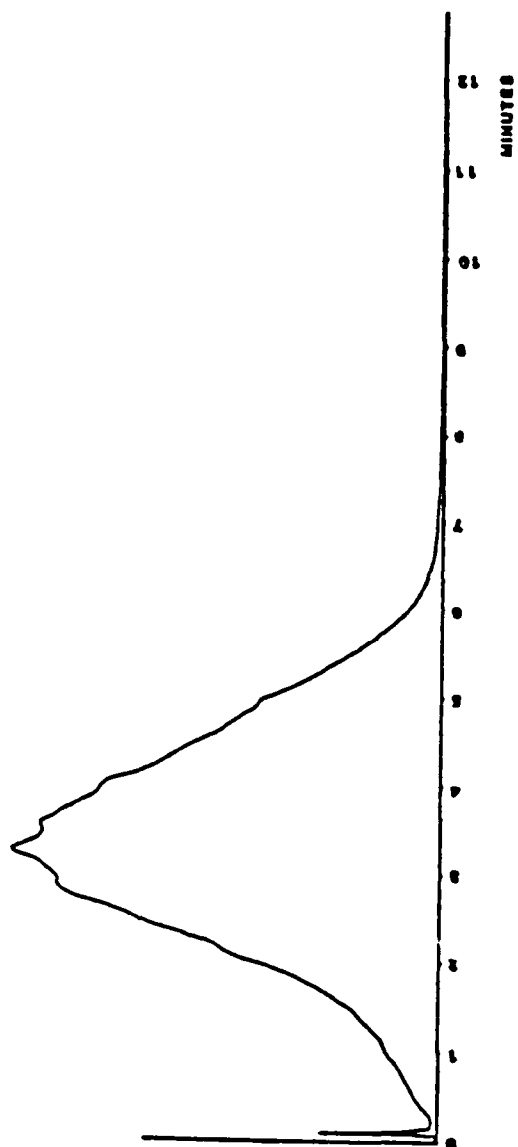
Figure 3.1 Chromatograms of Fog Oil and a n-Paraffin
Mixture for Two Oven Ramp Rates (continued)

3.2 Thermal Desorption

3.2.1 Automated Thermal Desorption

3.2.1.1 Instrument Description

A Perkin-Elmer ATD-50 Automatic Thermal Desorption Instrument was first used for thermal desorption of sample tubes. It provides automatic indexing and loading of fifty samples into a heated oven for desorption of the sample with carrier gas. An electronically cooled trap packed with Tenax-GC is provided for reconcentration of volatiles desorbed from the sample tube. The trap is then rapidly heated with carrier gas flowing to introduce the sample onto the chromatograph column in a very short time interval.

Sample tubes may be desorbed at temperatures ranging from 50°C to 250°C. The trap on the ATD-50 is maintained at a low temperature which may be set from -30°C to 30°C. The trap is fired for forty-five seconds to a high temperature which may be set from 50°C to 300°C at the start of each analysis to provide a sharp injection of sample to the chromatograph column. The sample is carried between the ATD-50 and the chromatograph by means of a heated line.

3.2.1.2 Desorption Method

The heated line from this instrument was coupled to the FID through a section of 1/16-in. stainless steel tubing to determine the nature of the sample injection when fog oil was desorbed from sample tubes. The chromatograph oven and detector block were maintained at 250°C to prevent sample from condensing in the oven. Samples in the ATD-50 were desorbed at 150°C, the valve box and transfer line were set at 150°C and the trap was cooled to -30°C and heated to 300°C. A plot of the detector output is shown in figure 3.2. The response appears as a series of evenly spaced peaks superimposed on a decaying exponential curve. Lower boiling samples, such as benzene produced a single sharp spike with very little tailing. Instrumentation of the transfer line with thermocouples indicated that it was only being maintained at 80°C. The oil was condensing on a portion of the heated line, and vaporizing as it was carried to a hotter section. This resulted in the cyclical variation of concentration at the detector. Replacement of the transfer line with another line wrapped with a Thermolyne tape heater eliminated the condensation problem.

There is carryover from one run to subsequent runs with the ATD-50 even with small quantities of volatile samples. This is due to residual sample remaining on the trap after the heating period. This is shown in figure 3.3 for a test mixture of n-paraffins. A sample tube was doped with the mixture and analyzed in the ATD-50. The subsequent runs are sequential trap firings with no sample added into the system. On the first sequential run about five percent of the sample remained on the trap. No provision is provided for purging and venting the trap between runs, or extending the trap heating period. The ATD-50 must be manually reprogrammed for multiple trap firing between sample analyses, or blank sample tubes may be alternated with exposed sample tubes. This would effectively double or triple the analysis time.

With the trap bypassed, the instrument can be used as a single stage desorption instrument. Sample is carried directly from the sample tube to the chromatograph column through the heated line. In this configuration, the ATD 50 was used successfully to desorb fog oil from sample tubes.

The ATD-50 has a error checking routine to check the integrity of the sample tube and instrument before desorbing the sample. Temperature parameters, pressurization of the tube, and mechanical malfunctions are all monitored. If an error is detected, the instrument shuts itself down. In practice, the instrument needed to be continuously monitored to prevent excessive downtime. Leakage of carrier gas and mechanical malfunctions were the most common problems and required time to isolate and fix. In addition, since the entire sample path is not maintained above the desorption temperature, sample would

TRAP FIRE

MINUTES

Figure 3.2 Desorption Profile of Oil Sample Using Perkin-
Elmer ATD-50 Automatic Thermal Desorption Unit

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(a) Sample Tube Desorption of n-Paraffin mixture

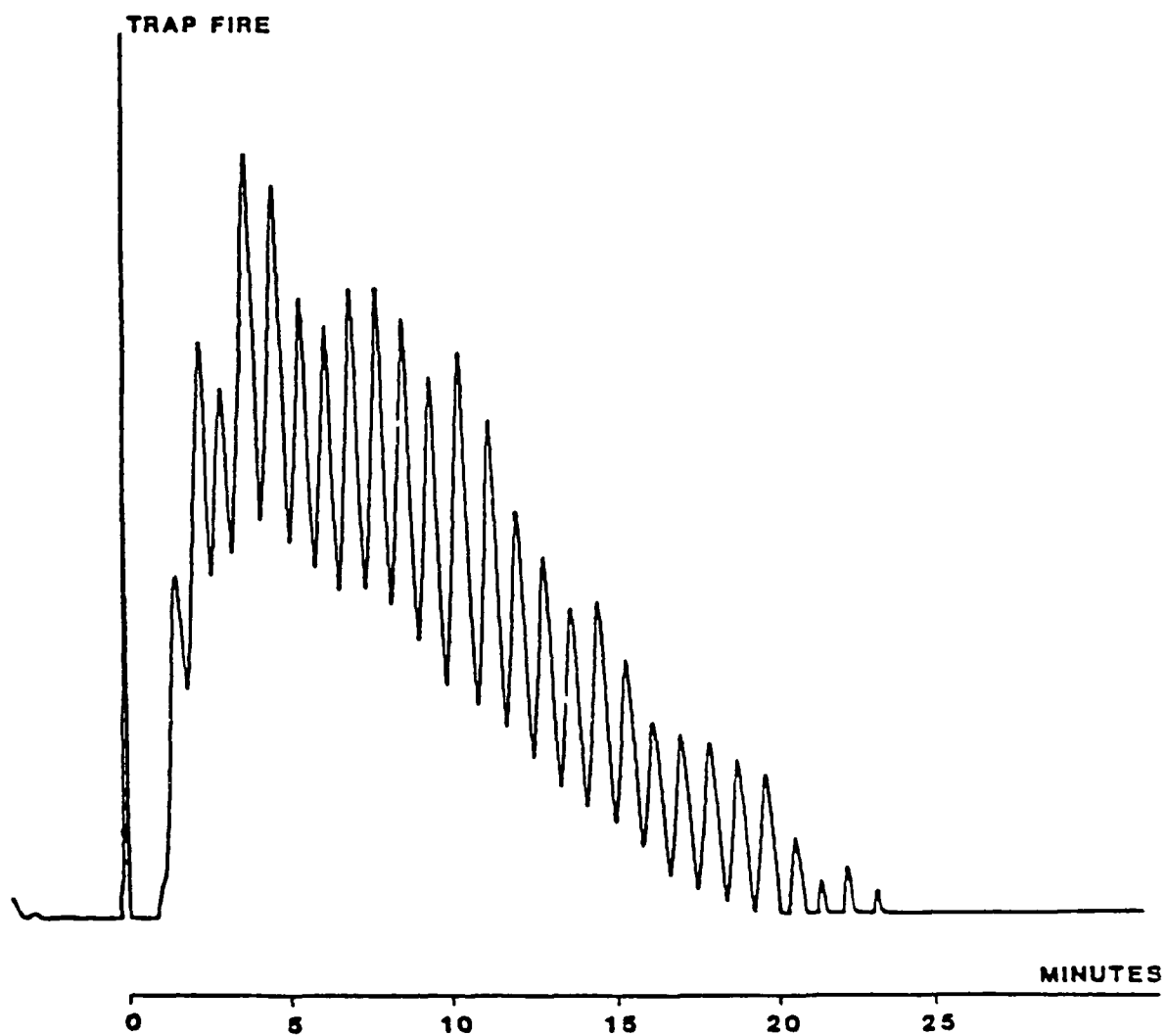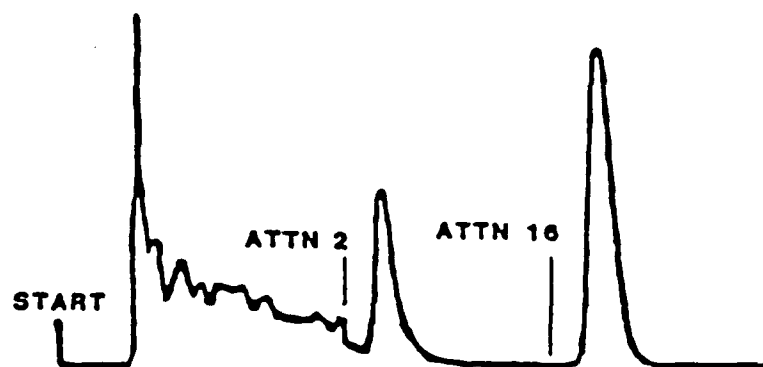(b) Second Firing of Cold Trap with Carryover of Sample
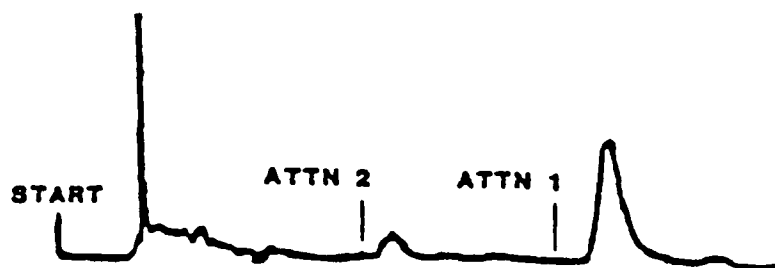
(c) Third Firing of Trap with Additional Carryover
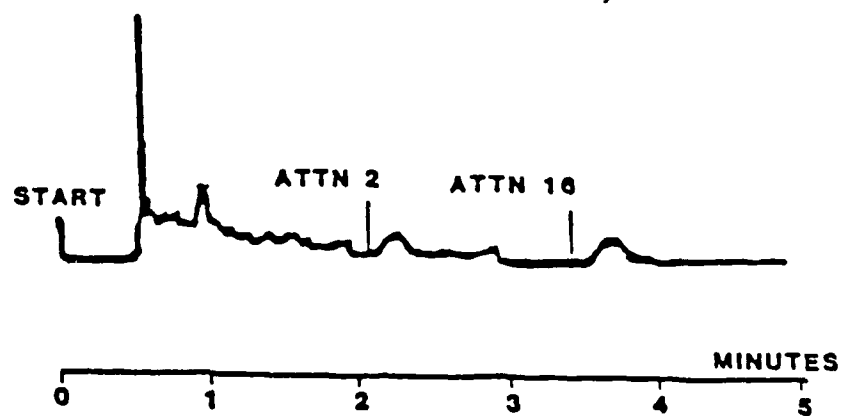
Figure 3.3 Carryover of Sample on the ATD-50 Cold Trap

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condense at these cooler points. This was especially a problem with the valved end caps used when desorbing the sample tubes. The end cap through which the sample is carried is not contained within the heated area, and is contaminated with sample after desorption. After each use it is necessary to disassemble and clean each valved end cap with solvent. It was decided an alternate, more reliable method would be used to desorb samples.

3.2.2 Injector Port Thermal Desorption

3.2.2.1 Injector Port Modification

Modification of the injector on the gas chromatograph to accommodate sample tubes proved to be an acceptable way to desorb the samples. The glass liner and spring were removed from the injector body. A 0.63 cm diameter by 8.9 cm long sample tube could then fit within the injector as shown in figure 3.4. The tube is heated to the injector block temperature which is set at 300°C.

The regular carrier gas inlet to the injector was capped. A 1/4 in Swagelock fitting through which carrier gas is supplied, replaced the septum and septum cap on the injector. Once heated in the injector, the tube is purged with carrier gas to carry the sample onto the column.

A series of Clippard diaphragm type solenoid controlled valves are used for switching carrier from the column to the injector for desorption. A twenty-four volt power supply and a Perkin-Elmer LCI-100 Laboratory Computing Integrator with a timed event option consisting of six SPST programmable relays is used for timing and switching the valves.

The valving setup is shown schematically in figure 3.5. The heated valve (6), is a Valco Instruments three port rotary valve for high temperature use that is pneumatically actuatated by two solenoid controlled valves supplied with clean dry air. Valves are in the position shown in the figure at the start and between analyses. The injector port may be opened for insertion or removal of a sample without interruption of carrier gas through the column.

3.2.2.2 Sample Analysis Method

For analysis of a sample, the injector port is opened and a sample tube inserted. A short cylindrical spring is inserted after the tube and the Swagelock fitting tightened. The spring holds the tube against the bottom of the injector so that all of the carrier gas must pass through the tube packing. Valve 2 is opened for a short interval to pressurize the injector port to the same level as the column head pressure and then closed. The automatic sequencing of valves, chromatograph oven temperature programming, and detector data acquisition is then initiated. The chromatograph oven is initially maintained isothermally at 150°C.

At the start, the heated valve is switched and pressure in the injector body and column head equalizes. Valve 1 is then switched to direct carrier gas through the sample tube, and sample is carried onto the columns. Valves 1 and 6 are switched back to their original position after all sample components have eluted from the column. The flow controller holds the flow rate through the system at 70 ml/min, despite changes in back pressure caused by the switching of valves1 and 6.

Also at the start, linear ramping of the oven temperature begins at 25°C/min to a final temperature of 330°C which is held until the end of the run. After the run, the oven is again cooled to the initial temperature of 150°C. At eighteen minutes data acquisition is stopped and integrated peak area reports are printed. Once the oven has finished cooling, another analysis may be made.

The sample desorbed in the injector passes through a flow splitter and onto one of two columns. Both columns are 1.2 m long, 1/8 in diameter stainless steel packed with 3% Dexsil 300 on 100/120 mesh Chromasorb W HP. Dexsil 300 is a nonpolar silicon oil similar to many other stationary phases suitable for separation of moderate weight hydrocarbons. Chromasorb W HP is an inert, high purity support made

PURGE FLOW
INLET

SWAGELOCK NUT
TO REPLACE
SEPTUM CAP

SAMPLE TUBE

INJECTOR BODY

CARRIER GAS
INLET (CAPPED)

TO COLUMN

Figure 3.4 Injector Body Modification for a Sample Tube Thermal Desorption
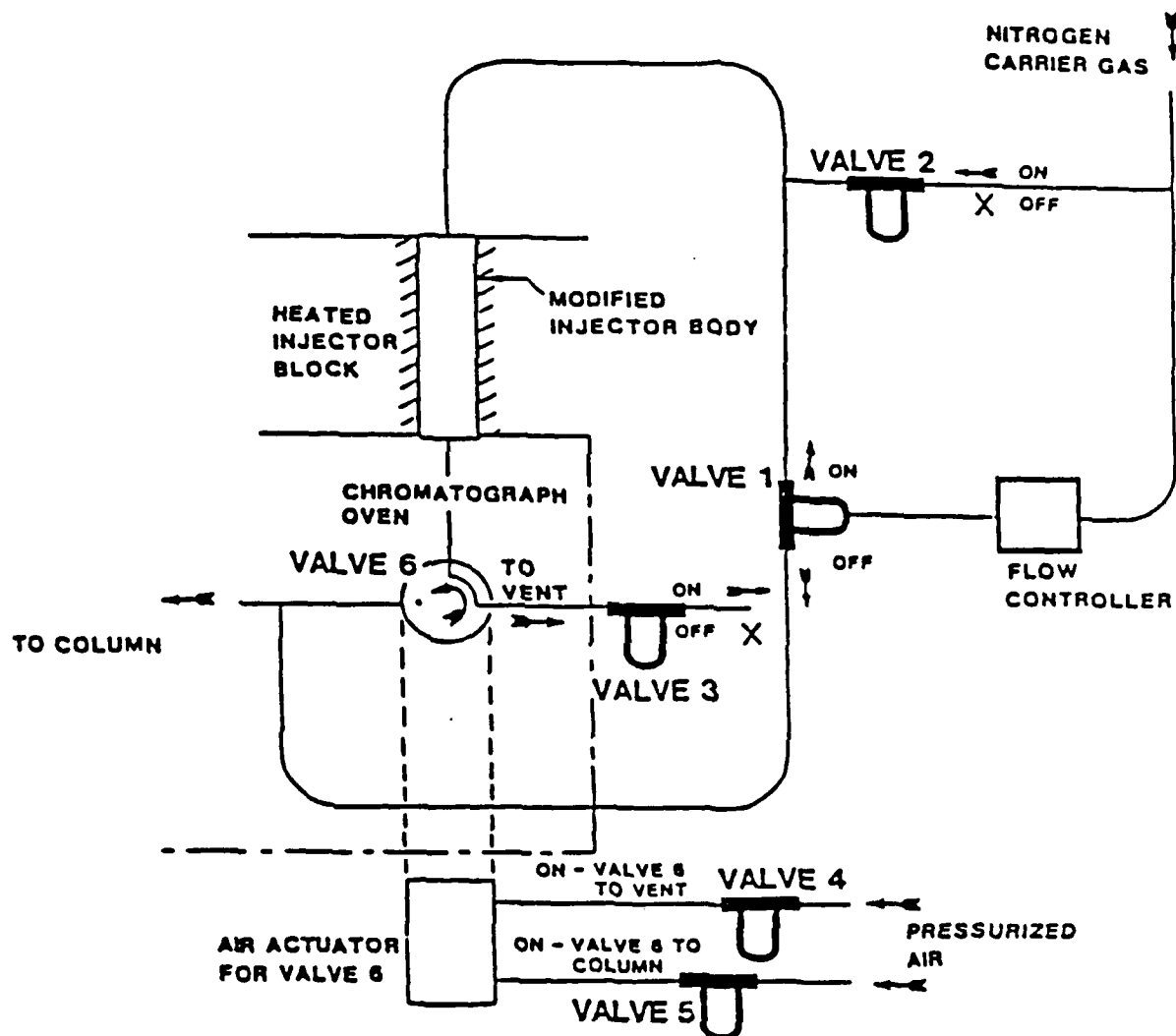
Figure 3.5 Schematic of Injector Tube Thermal Desorption
Valving Arrangement and Carrier Gas Flow.

from diatomaceous earth. Column 1 is connected to the flame ionization detector and has a flow rate of 40 ml/min. Column 2 is vented through a capillary flow restrictor and has a flow rate of 30 ml/min. Two columns are used in order to maintain a high flow r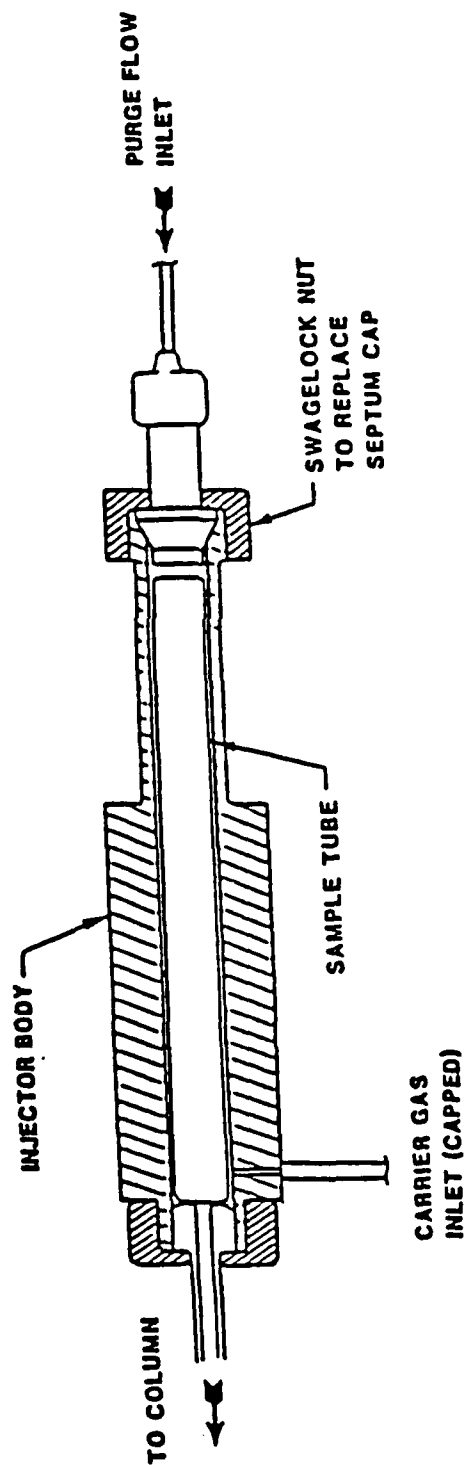ate through the sample tube, and an acceptable flow rate through the column. Because both columns are the same type, they have identical back pressure versus temperature relationships and the split ratio will remain the same with changing oven temperature.

3.2.2.3 Determination of Analysis Parameters

In the analysis of the many thousands of oil samples we have collected, the speed of analysis is an important criterion. Accurate, understandable, and repeatable results are also very important. Many parameters may be varied in this system to speed up the analysis, while still maintaining the integrity of the results. Some have a greater effect, and some must meet certain constraints. A timing chart of the desorption method is given in figure 3.6 that illustrates many of these parameters. A table of operating parameters selected for the analysis of oil samples is given in table 3.2. These parameters were determined from previous work, and by experimentation.

Temperature has the greatest effect on the analysis. The sample tubes are desorbed at 300°C, which is 30°C below the maximum recommended temperature for the adsorbent. Above this temperature, the Tenax-GC adsorbent begins to decompose and at lower temperatures desorption is slower. The detector is maintained at 375°C to prevent contamination by the condensation of sample in the detector. The maximum oven temperature is 330°C, slightly higher than the maximum temperature at which the highest boiling oil components elute from the column.

The lower oven temperature should be as high as possible. Much of the time between runs is taken up in cooling the chromatograph oven. Several chromatograms are given in figure 3.7 in which the initial oven temperature was set in increments from 125°C to 225°C with other parameters held constant. One microliter of oil was desorbed from a sample tube in each case. The initial temperature is held for six minutes before increasing at 25°C/min to 330°C.

An interesting trend is observed. At the lower temperatures a peak appears at about eight minutes. This is the period when the oven temperature is ramping to elute the oil. As the initial temperature increases, this peak decreases in size while another appears much earlier in time.

This effect is due to the partition coefficient changing with temperature, and other nonlinear effects. At 125°C and 150°C, the sample is fully absorbed onto the stationary phase. At the intermediate temperatures of 175°C and 200°C, part of the sample is absorbed, but the stationary phase on the column is saturated and a portion of the sample is carried off the end of the column. The absorbed portion of the oil then elutes when the column temperature is raised. At 225°C, almost all of the sample passes through the column before the temperature of the column is raised. Under these conditions, using an initial temperature of 150°C or less is necessary to produce understandable results and eliminate the psuedo-peaks early in the analysis.

Cooling of the oven from 330°C to 150°C after each analysis takes approximately six minutes. During this period an air cylinder automatically opens the chromatograph oven lid to permit quicker cooling of the system. Modification of the oven lid opener using an auxiliary air cylinder reduced the cooling time to four minutes.

Another parameter of interest is the time allowed to purge the oil from the sample tube onto the column before raising the column temperature. We refer to this as the isothermal time. A series of superimposed chromatograms shown in figure 3.8 show the effect of varying the isothermal time from zero to six minutes. All of the chromatograms were produced with one microgram of oil.

One of the effects of this variation of isothermal time may be seen by the relative amplitudes of the oil components which appear as partially separated peaks near the top of each chromatogram. The first peaks to elute, which consists of lighter components, becomes progressively smaller compared to later

43
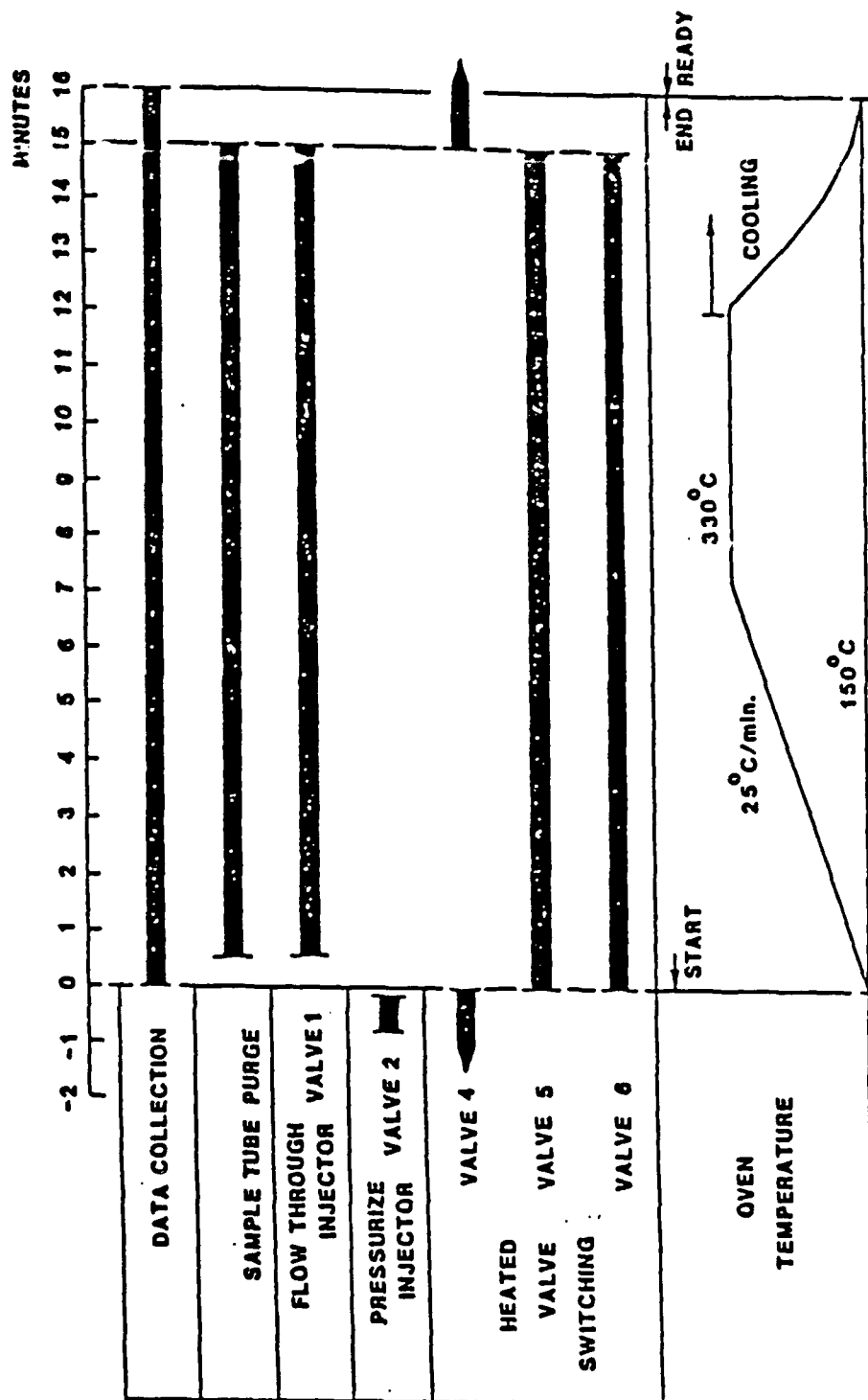
Figure 3.6 Timing Diagram for the Thermal Desorption Method

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Table 3.2 Operating Parameters for Analysis of Fog Oil using Thermal Desorption

Detector:	FID
Column:	1.2 m, 0.22 cm i.d., 0.32 o.d., 3%
	Dexsil 300 GC on Chromasorb WHP
Temperatures	
Sample Inlet:	300°C
Detector:	375°C
Column:	
Initial:	150°C
Rate:	25°C/min
Final:	330°C, hold for 4.8 min
Carrier gas:	Nitrogen, Ultrapure
Flow rate	
Column:	40 ml/min
Inlet:	70 ml/min
Split Ratio:	1 : 0.75
Desorption Time	
Start:	0.5 min
End:	15 min
Analysis Time:	12 min
Cycle time:	16 min
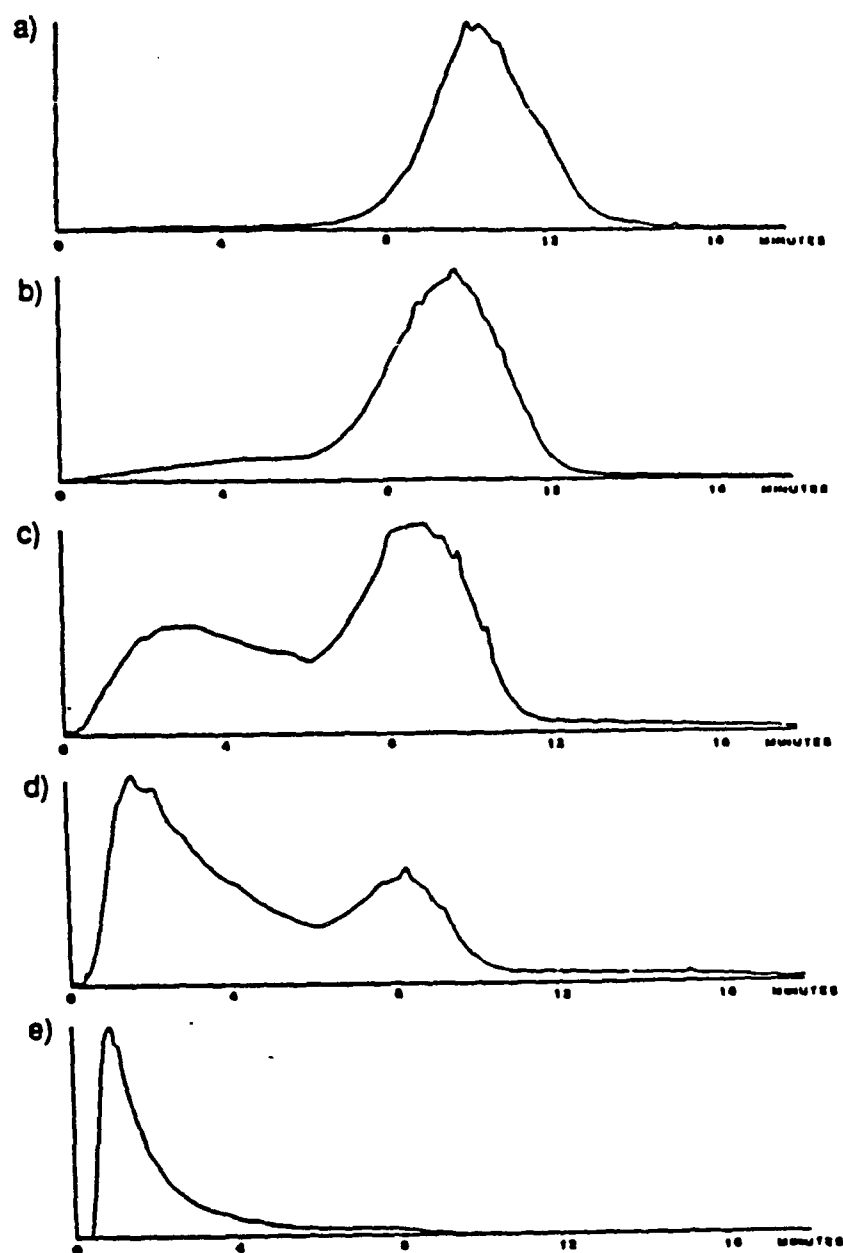
Figure 3.7 Series of Chromatograms for which the Initial
Oven Temperature is set at a) 125°C, b) 150°C,
c) 175°C, d) 200°C, and e) 225°C

46
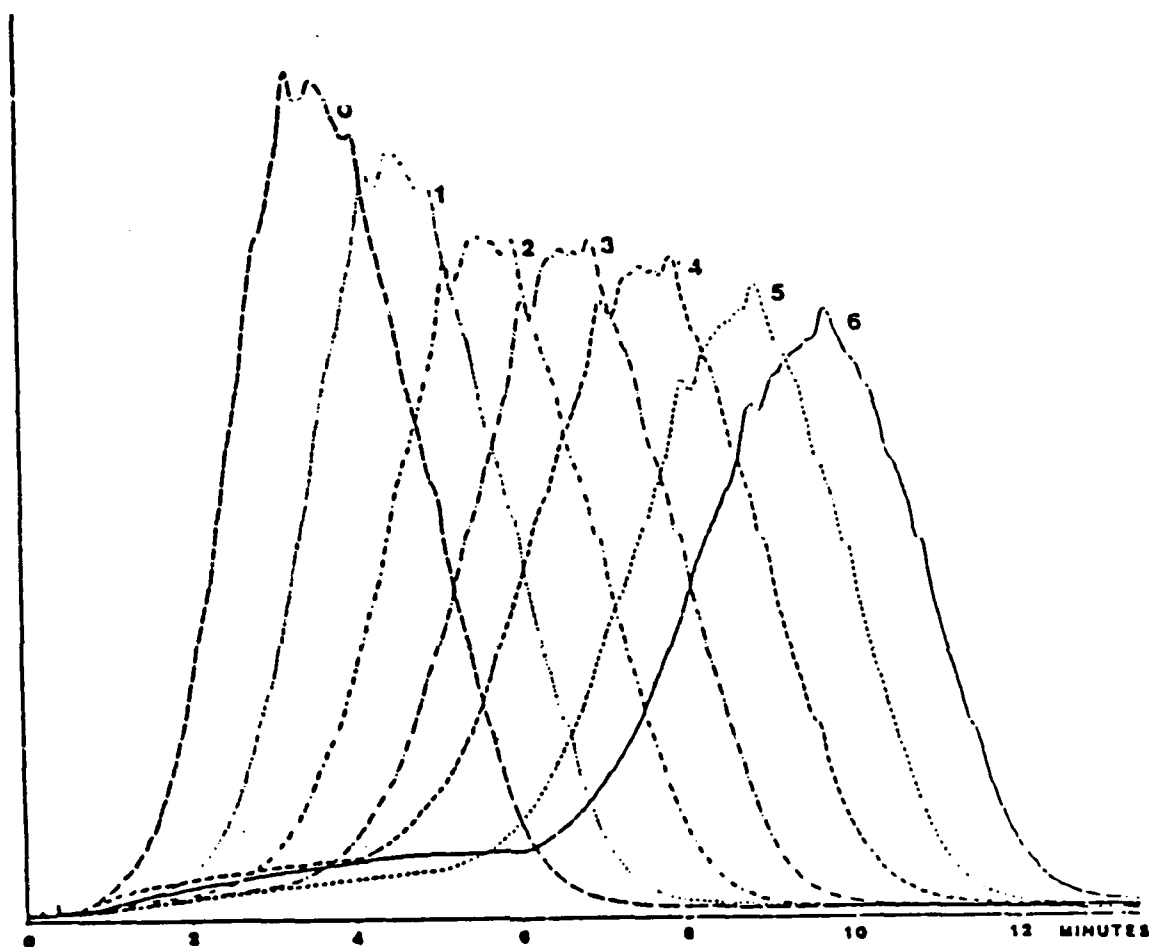
Figure 3.8 Series of Chromatograms Showing the Effect of
Holding the Initial Oven Temperature Constant for
a Period of Zero to Six Minutes Before Ramping
the Temperature at 25°C/min

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eluting peaks as the isothermal time is lengthened. This is caused by the lighter components passing off the column before the column temperature is raised. The general shape of the chromatogram is also broader and shorter with increasing isothermal time.

Ramping the temperature at the start of sample desorption produces a better, more resolved chromatogram (although never resolved to the point of separate, visible peaks). It also saves considerable analysis time which is evident from looking at the analysis times of each run in figure 3.8.

The effect of rate of temperature increase is shown in figure 3.9. All the chromatograms were made with one microliter of oil. The oven was initially at 150°C. The oil eluted fastest for the greatest rate of temperature increase. There is not much difference in the resolution of the oil between the chromatograms. At the lowest rate, the oil exhibits tailing at extended time. For the other rates, the chromatograms are nearly symmetrical.

3.3 Sampling Apparatus

3.3.1 Adsorbent Filled Tubes

The body of the adsorbent filled stainless steel tubes we are using are 0.63 cm outside diameter, 0.46 cm inside diameter, and 8.9 cm long. A circumferential groove is pressed into the tube 1.5 cm from one end leaving a ridge on the inside of the tube. A 0.47 cm diameter 100 mesh stainless steel screen is seated on this groove and the tube is filled with 0.20 g of 60/80 mesh Tenax GC. Another screen is pressed into the tube to a depth of 0.7 cm. This give a 6.7 cm long bed of adsorbent in each tube.

The tubes must be conditioned before use by heating and purging the adsorbent with carrier gas. This may be done in the heated injector port. Adsorbent filled tubes are loaded into the port. Valves 2 and 3 are opened with the heated valve (6) in the position shown in figure 3.5. This allows carrier gas to flow through the sample tube and purge extraneous volatiles from the adsorbent before exposure of the tube in the atmosphere. A flow restrictor in the vent line limits the flow to about 100 ml/min and a charcoal filled trap absorbs the vapor from the carrier stream before venting into the laboratory. About thirty minutes of conditioning is necessary for each tube.

3.3.2 Filtration Methods

The glass fiber filters are used in cassette holders. The cassette holders are commercially available in a multitude of sizes from Millipore Corp. and Gelman Instrument Co. , among others. They consist of a backup holder, a filter retaining gasket, and a cover that holds the filter in place. They are usually used with membrane filters, but may also be used with glass fiber filters. The larger size filters used in cassette holders permit higher sampling rates and capacity for a given filter face velocity. The 2.4 cm diameter filters may be easily folded and placed in an empty sampling tube for analysis. Cassettes and filters of 37 mm diameter were used in our field experiments and a half-fraction of the filter was analyzed. The other half of the filter was used, if necessary, to replicate the analysis.

Larger filters, may be extracted with liquid. Hexane is added to the vial and it is agitated. A stainless steel sampling tube that has been packed with glass wool and capped at one end with a stainless steel end cap is filled with the hexane solution. The hexane is evaporated, leaving the oil on the glass wool. If more solution remains in the vial, the stainless steel tube may again be filled with solution and evaporated. After complete evaporation of the hexane, the sample tube is analyzed.

3.3.3 Cascade Impactors

The cascade impactors we are using are from In-Tox Products. They have seven stages with cut points of 0.33, 0.71, 1.05, 1.58, 2.1, 3.0, and 4.6 μm at a flow rate of 1 l/min. The impactor stages hold 2.4 cm circular microscope slide covers on which the aerosol is collected. For collection of the liquid oil
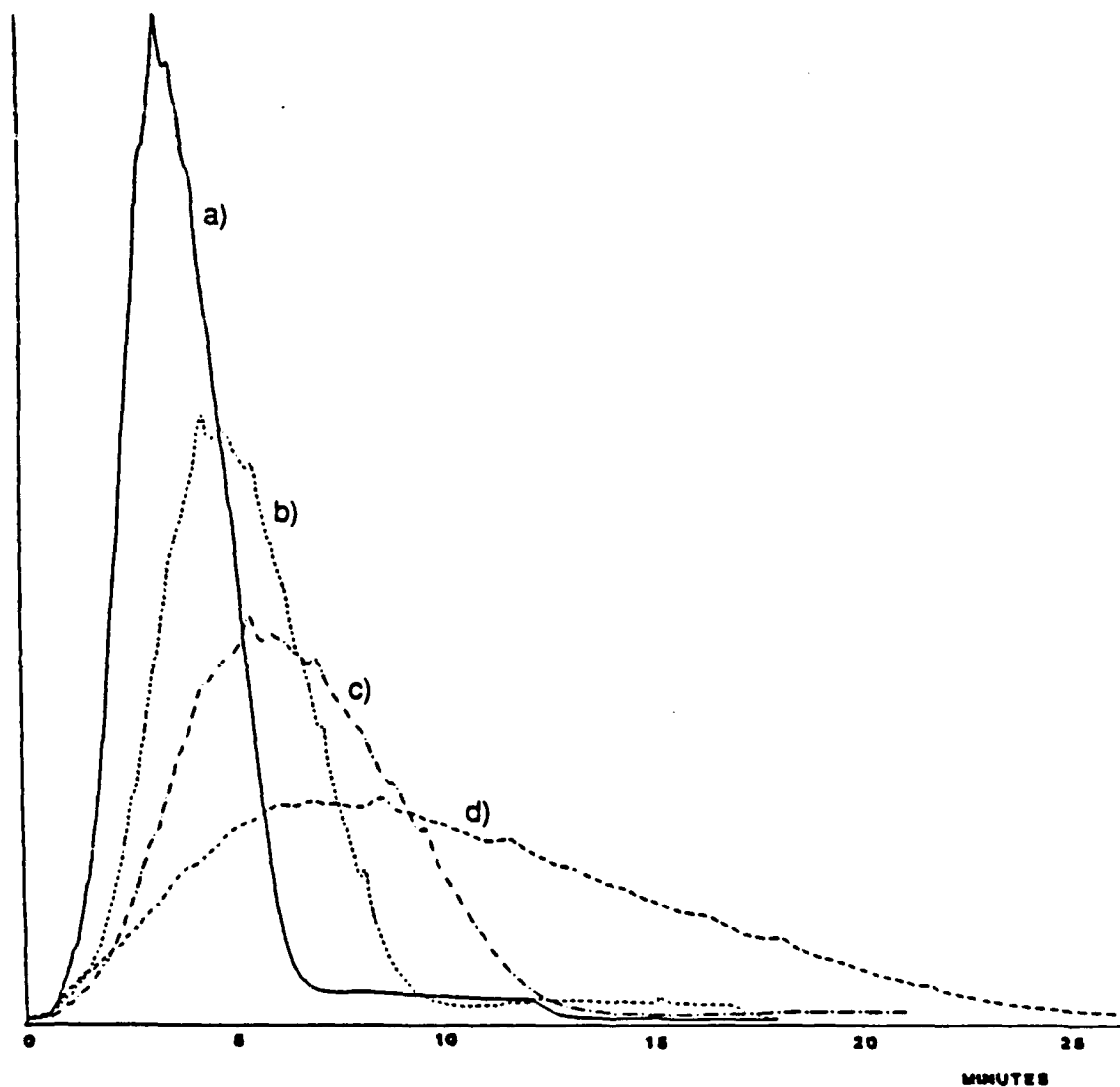
Figure 3.9 Series of Chromatograms Showing the Effect of
Varying the Rate of Temperature Increase. Runs
were made at a) 25°C/min, b) 15°C/min,
c) 10°C/min, and d) 4°C/min

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aerosol, the plates are left dry. Collected oil is clearly visible on the smooth glass surface under bright light.

For analysis, the glass cover slips are transferred to vials and extracted with hexane for analysis. The method is similar to liquid extraction of the filters. Since cascade impactors are only used for aerosol size distribution measurements, and not total particulate mass measurements, only relative amounts of oil on the stages within a cascade impactor are important. All of the stages from an individual impactor are prepared and analyzed as a set, and no external calibration measurements are needed.

Alternately, the stages of the impactor are wiped clean with a glass fiber filter, and the filter is directly analyzed. This method produced results comparable to the hexane extraction, with less sample handling, and fewer chances for error.

3.3.4 Sampler Aspiration Methods

The flow rate through most of the filter samplers is monitored with a rotameter mounted between the filter and the vacuum pump, which will give a continuous and direct reading of the flow rate. For the filters, errors in the flow rate due to the lower absolute pressure upstream from the sampler were small. The flow was also steady in time, with no evidence of increased back pressure due to clogging.

The flow rates through some of the sampling devices are controlled using calibrated choked flow restrictors. The restrictor is mounted in the vacuum line between the sampling device and the vacuum pump. When the absolute pressure ratio across such a device is greater than a given value, the flow is choked, and the nondimensional mass flow rate m_*, is constant. The value m_* is given by

$$m_* = \frac{\omega\sqrt{RT}}{PA} = \text{constant} \qquad (3.1)$$

From a reference condition, the actual mass flow can be calculated by measuring the temperature and pressure upstream from the flow restrictor:

$$\omega = \omega_{ref}\left[\frac{P}{P_{ref}}\right]\sqrt{\frac{T_{ref}}{T}} \qquad (3.2)$$

Both temperature and pressure are in absolute units in equation 3.2. Choked flow will always occur for absolute pressure ratios greater than 0.5283 in air. It may also occur for a lower ratio depending on the restrictor geometry.

3.4 Smoke Generation

The Army smoke generator for field use consumes large quantities of oil that would present disposal problems if used in the laboratory. A laboratory smoke generator for creating fog oil aerosol to evaluate sampling methods was constructed. The laboratory generator uses 20 ml of oil an hour. A diagram of the generator is shown in figure 3.10. It is similar in design to a chromatograph injection port.

The generator is constructed of stainless steel tubing and Swagelock fittings. Heavy walled copper tubing around the stainless steel serves as heat storage to maintain an even temperature throughout the generator. A thermocouple is mounted within the generator to monitor the temperature.

50
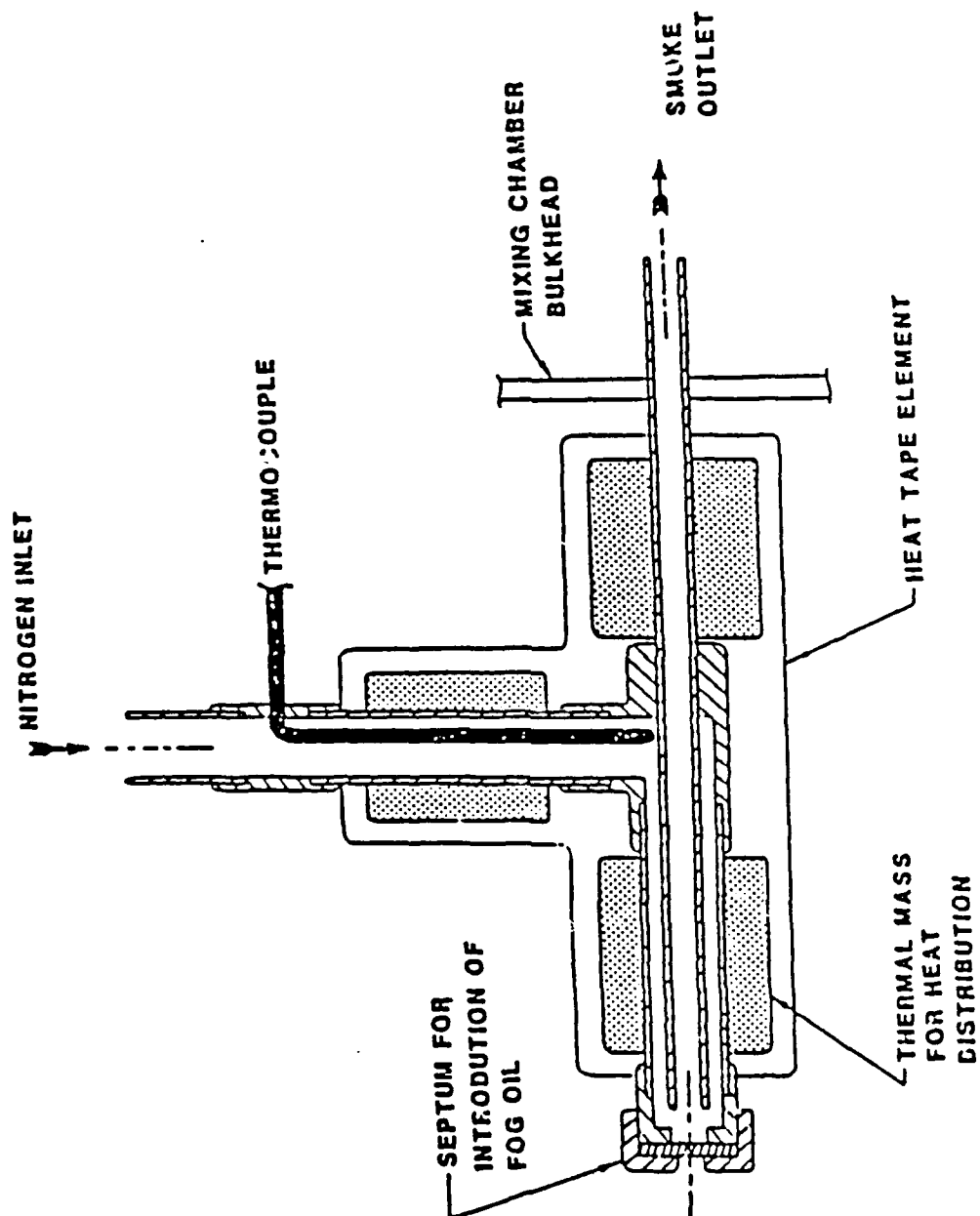
Figure 3.10 Schematic of Laboratory Smoke Generator

NITROGEN INLET

THERMOCOUPLE

SEPTUM FOR INTRODUTION OF FOG OIL

MIXING CHAMBER BULKHEAD

SMOKE OUTLET

HEAT TAPE ELEMENT

THERMAL MASS FOR HEAT DISTRIBUTION

The body of the generator is wrapped with a Thermolyne heat tape which is controlled by a 120 volt variable transformer.

Nitrogen is introduced into the generator through the tee. It flow up the outside 1/4 in tube, and back through the center 1/8 in tube. Oil is introduced into the 1/8 in center tube through a 3/8 in septum using a syringe. The septum holder is a 1/4 in Swagelock union, with the a front ferrule and a nut holding the septum in place. For short puffs of smoke, the oil is manually injected. For operation of up to a half-hour, a motor-driven syringe pump is used.

The oil vaporizes in the center tube and is carried with the nitrogen to the generator outlet, where it cools and condenses to a dense white fog. The outlet of the generator is directed into an aluminum enclosure with a removable plexiglass top where it is diluted and mixed with air. The fog exits from the chamber through a 20 cm long, 8 cm diameter vertical port, where it is also sampled. The excess smoke is removed from the lab through an exhaust hood.

4.0 EXPERIMENTAL RESULTS

In testing of the thermal desorption analysis system, it was necessary to calibrate the system and determine the linear operating range of the detector. The minimum detectability of the fog oil and the interference of various atmospheric pollutants with the detection of oil also needed to be investigated. The chemical nature of the fog-oil smoke and the relative fractions of liquid aerosol and vapor phases under ambient conditions were also found. Glass fiber filter and Tenax-GC adsorbent packed tubes were used for collection of the fog oil and the efficiency and effectiveness of each sampling method under various conditions was investigated. Cascade impactor measurements were made to determine the particle size distribution of the fog-oil smoke.

4.1 System Calibration

4.1.1 Calibration Method

Calibration of the detector response was accomplished by running a series of sample tubes doped with a known quantity of fog oil. Each tube had a stainless steel screen mounted within one end. Injections of oil onto the screen were made using either a one or a ten microliter Hamilton syringe. The tube was then inserted into the chromatograph injector for analysis.

The one microliter syringe has a plunger which extends to the tip of the needle. This helps in transferring all of the oil to the sample tube. In the larger syringe, some of the oil is left within the needle. Plots of integrated detector response versus quantity of oil using this syringe give a nonzero intercept of 0.36 mg. This is the amount of oil left within the syringe needle after an injection. The results found when using this syringe are adjusted by this amount.

4.1.2 Calibration Results

A plot of integrated area under the chromatograms versus mass of oil is given in figure 4.1. The integrated area is in arbitrary units assigned by the integrating device. The response is linear over the useful range. The multiple injection calibration method used is necessary because of the many components in the fog oil and the partial separation of the oil on the column. It appears to work very well, most likely because of the insensitivity of the FID to differences in the chemical nature of various organic chemical species.

The effect of system overloading is due to two major effects and shows up in chromatograms of the oil at higher mass concentrations. At lower levels the chromatograms appear normal as shown in figure 4.2a. With higher amounts of oil, chromatograms are produced as shown in figure 4.2b. An extraneous peak appears about six minutes into the run, due to continued desorption of oil from the tube after the column temperature is raised. In addition, after the analysis when the tube is removed from the injector, a small amount of smoke may come from the tube and the injector opening indicating that desorption of the sample was not complete. The incomplete desorption increases the error in measuring the quantity of oil. In addition, at still higher dosages of oil, the peak signal level sometimes exceeds the voltage limits of the detector amplifier. The clipping of the amplifier may be overcome by changing the attenuation level of the detector.

The reason for the remaining oil in the tubes and the extraneous peak in the chromatograms is that all of the oil is not being quickly vaporized and swept from the tube. If the initial oven temperature is lowered, the extraneous peak disappears because the additional time allows nearly all the oil to be purged onto the column before the column temperature is raised. Other methods that help increase the upper mass limit include extending the analysis time, reducing the rate of oven temperature increase during the run, and holding the oven temperature constant for a short period at the beginning of the analysis.

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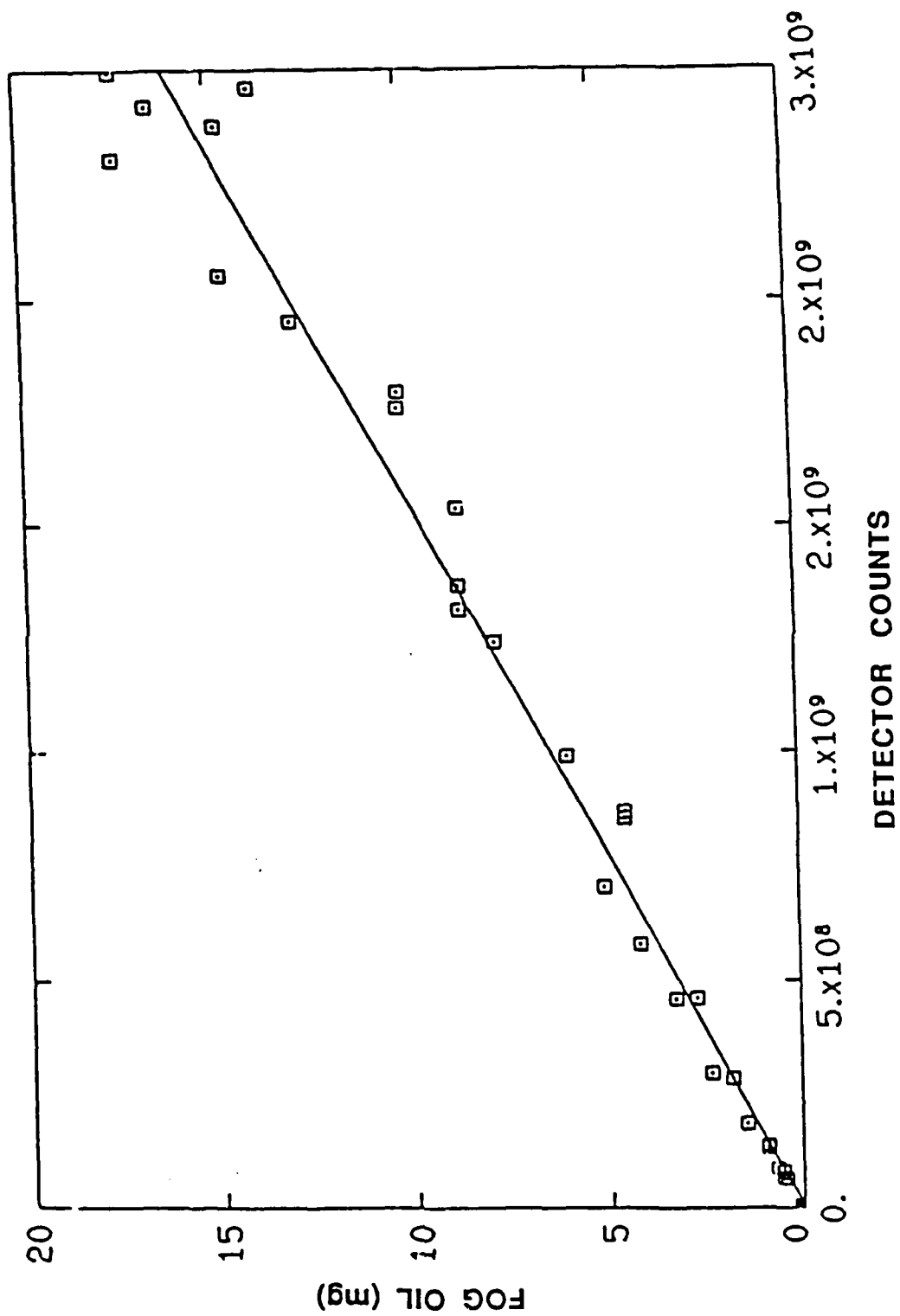
Figure 4.1 Calibration Results for the Analysis of Fog Oil by Thermal Desorption
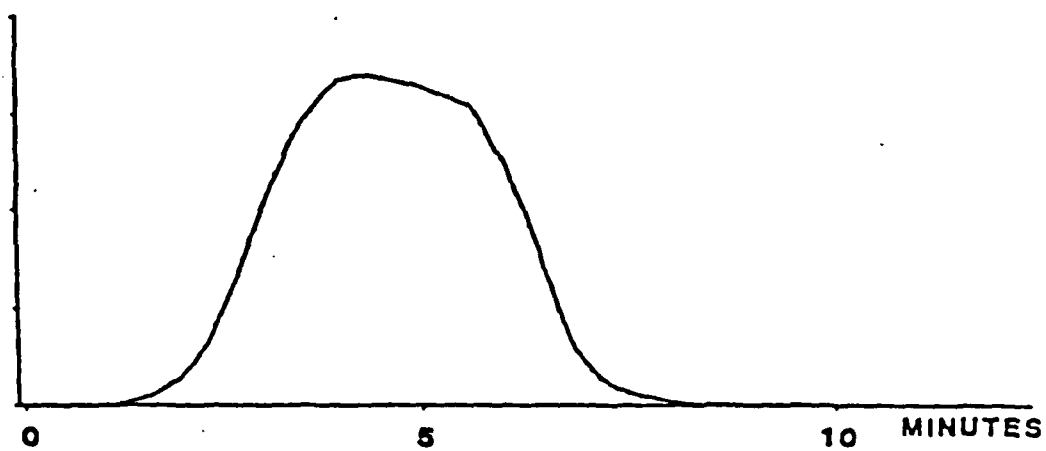
a) Low Levels of Oll (5mg)
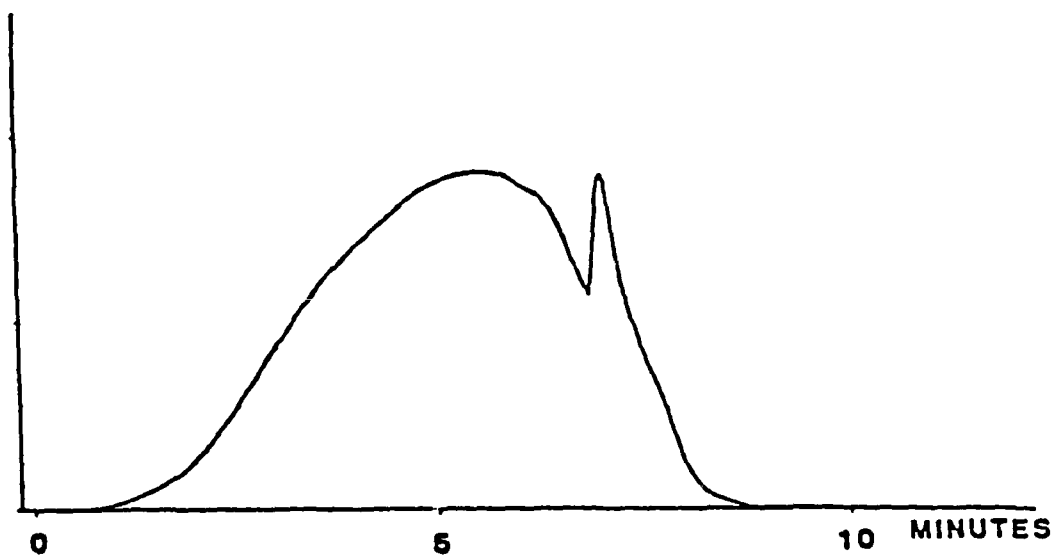
b) Higher Amounts of Oll (25mg)

Figure 4.2 Chromatograms of Oll at High and Low Levels
Indicating Saturation of the Analysis System

All of these methods increase the overall analysis time which is undesirable and also unnecessary for the lower (and more likely) oil concentrations. Additional methods that would increase the linear range of the system are possible but would require hardware modifications.

One of the simplest hardware modifications would be to change the split ratio of the column. Using a longer column or increasing the mobile phase loading on the column would also increase the column capacity and linear range. These methods would then require recalibration of the detector, but the system response would still be linear.

For sample sizes of less than about fifteen milligrams, the system response is very good. The data may be simply fitted with a linear equation of the form:

$$mass(mg) = counts \times 6.577 \times 10^{-9} \qquad (4.1)$$

Measurements in this range are within +-7% of the response curve with a confidence interval of 50%. For quantities smaller than 0.05 mg, error is due to the difficulty in injecting the small quantity of oil onto the sample tube, and not because of the system response. Variations in the calibration occur over time, and the calibration constant is determined regularly.

4.1.3 Theoretical Minimum Detection Level

The algorithms within the Perkin-Elmer LCI-100 Integrator indicate that the minimum area sensitivity of the system over an analysis cycle is 6 integration units. This is a measurement of the integral of the system noise level. For a signal to noise ratio of 2, an oil sample would have an area of 12. This corresponds to an oil sample size of 1.2×10^{-7} mg. In practice, it is very difficult to make a measurement of this size with atmospheric samplers because of background contamination levels or atmospheric background levels of interfering compounds.

The flame ionization detector which responds to the fog oil will also respond to other organic compounds. The lower detection limit of the fog oil will depend on the background concentration of hydrocarbons in the atmosphere which are in a similar molecular weight range as the fog oil. Contamination levels of the samplers which will occur in handling and analysis are also important.

In initial tests, filter cassettes for particulate collection backed with Tenax-GC adsorbent tubes were used outdoors and in the laboratory to determine the background level of interfering compounds. The various samplers were aspirated at flow rates from 0.5 liters per minute to several liters per minute for periods of time from 20 minutes to several hours.

All of the filters in this series of tests indicated an interference level of about 0.07 mg of oil. A set of adsorbent samplers with extensive conditioning and extreme care to ensure little contamination indicated a uniform background level of about 0.04 mg of oil. Another group of adsorbent samplers with less extensive conditioning and routine handling precautions to prevent contamination had a background level of 0.83 mg which is significantly higher than the first group of samplers. Unfortunately, all of the Tenax samplers used at the first field dispersion study at Dugway Proving Ground were contaminated with the higher background level, putting severe constraints on the minimum detectable concentration of smoke for this study. Later studies, which used the filter samplers, did not have the same problems.

The amounts of sample detected on the background samplers resulted from contamination of the samplers, despite reasonable care to prevent this contamination during sampling or analysis. The ambient background levels of interfering compounds were much lower than the interference level and did not show up in these tests.

In a later test of outdoor background levels of interfering compounds, several steps were taken to further reduce the contamination of the samples and improve the detection of the background aerosol. The background level of the Tenax sample tubes could not be significantly improved under these conditions. The filter background level could, however, be improved. New filter cassette housings were used and the empty sample tubes into which the filters are loaded and stored prior to analysis were heated for several days at $200^{\circ}C$ to evaporate volatile compounds from their surface. To collect a larger aerosol sample, two filters were aspirated outdoors for a period of several days at flow rates of 0.44 liters per minute and 0.96 liters per minute, respectively. The weather during this period was clear and dry.

After the aspiration period, the surface of each of the filters was evenly coated with a layer of fine, gray aerosol. The detectable level of interfering compounds on the filters was 0.20 mg and 0.42 mg respectively for each of the two flow rates. This corresponds to a background concentration of 1.6×10^{-4} mg/m^3. After analysis, the appearance of the filter when unloaded from the analysis tube was similar to its appearance before analysis. Apparently much of the collected material on the filters was not volatile and thus not subject to analysis by thermal desorption. The care necessary to achieve this level of detection may not be possible under field conditions.

Weather conditions, vegetation, industrial activity, and vehicular traffic will all contribute to the local background measurement. It is likely that the measured value of background aerosol will vary widely. For a sampler aspirated at 1 liters per minute for an hour at the background level found in the above tests, the collected mass would amount to only 10^{-2} mg. Even if the background aerosol level is significantly higher, it is likely that contamination of samples in routine handling or analysis will have a much greater effect on the minimum detection level.

4.2 Fog-Oil Smoke Characteristics

The characteristics of the smoke generated using the laboratory smoke generator were studied and compared with field generator results using various sampling methods. The laboratory generator was operated at a nitrogen flow rate of 2 liters per minute with oil consumption of between 5 and 12 ml/hr. The generator was heated to a steady operating temperature of $420^{\circ}C$ before initiating oil flow. The smoke was directed into the dilution chamber and mixed with clean dry air flowing at a rate of 12 liters per hour. All sampling of the laboratory smoke was done at the exit port of the dilution chamber.

4.2.1 Chemical Changes

The limited component resolution of the analysis system does not allow the identification of individual oil components and therefore the presence or absence of individual oil components through the generation process can not be determined. However, chromatograms produced using smoke samples from the laboratory generator, the M3A3E3 field generator, and the raw fog oil are nearly identical in appearance. Gross changes in the oil which may be detected from these chromatograms are negligible.

4.2.2 Aerosol - Vapor Characteristics

For study of the particle - vapor characteristics of the oil-fog smoke, 2.4 cm glass fiber filter cassettes backed with Tenax-GC adsorbent filled tubes were used. The particulate fraction of the smoke is collected on the filter, while vapors that pass through the filter are collected on the adsorbent. Low flow rates through the samplers were used to avoid evaporation effects and insure high efficiency collection. Analysis of the samplers showed that most of the oil was collected on the filter and a small fraction of the lighter molecular weight components were collected on the Tenax-GC adsorbent. Chromatograms of the particulate and vapor fractions of the oil are given in figure 4.3. From these chromatograms it is evident that there is a partitioning of the oil between vapor and liquid aerosol which depends on the boiling point of the sample constituents. The partition occurs at a boiling point of about $275^{\circ}C$, or at a molecular weight corresponding to tridecane (C_{13}). The amplitude scale on each chromatogram indicate the relative

3.0 VOLTS

1.5

0.0

0   2   4   6   8   10   12
MINUTES

a) Filter Analysis

0.10 VOLTS

0.05

0.00

0   2   4   6   8   10   12
MINUTES

b) Adsorbent Analysis
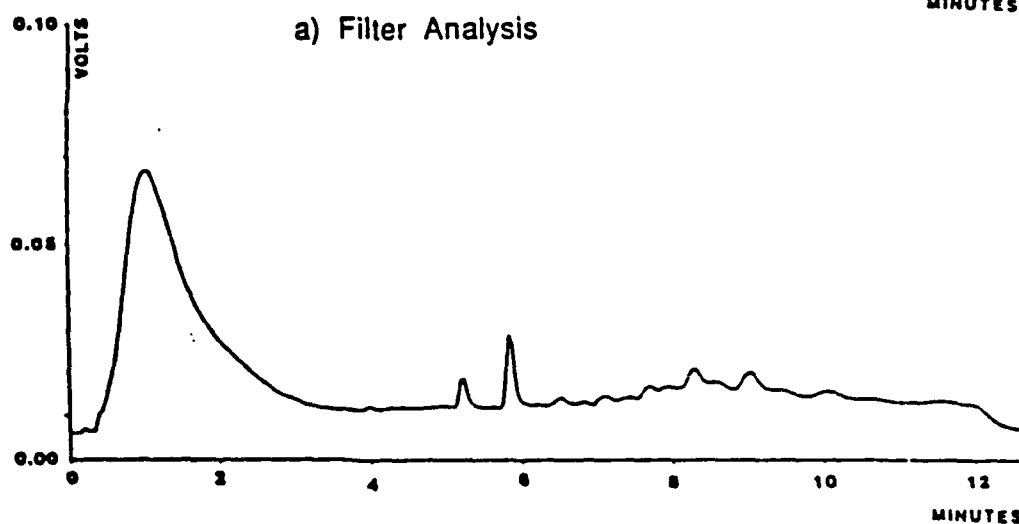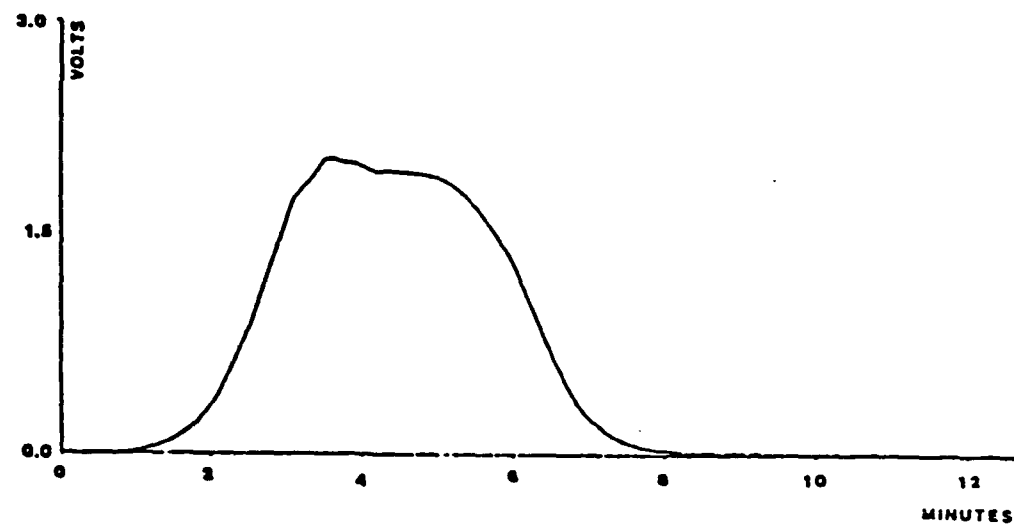
Figure 4.3 Chromatograms from Analysis of a Filter Cassette
backed by a Tenax-GC Adsorbent Tube

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amounts of aerosol and vapor. Comparing the integrated area of these chromatograms shows that about 99% of the sample was collected on the filter.

4.2.3 Particulate Size Distribution

The particulate size distribution of the laboratory aerosol was measured using an In-Tox Products cascade impactor. The impactor was aspirated at one liter per minute using a choked flow orifice and correcting for the pressure drop through the impactor. The instrument was aspirated for several minutes in the laboratory fog-oil smoke. After exposure, oil was visible under direct light on the impaction plates. At low levels the oil appears as a fine mist on the stage surface. At higher loadings the oil coalesces into small droplets on the stage and is radially blown from under the impactor jet on each stage. The impactor was considered overloaded only if oil ran over the edge of the stage.

The mass mean aerodynamic diameter of the aerosol was typically around 0.8 μm. The aerosol from the field generator is in the same size range during normal operation. The size distribution of the aerosol from the laboratory generator depends upon the generator operation. This was also the case for the field generator according to Katz et al. (1980). For both the field generator and the laboratory generator, lower oil flow rates will produce an aerosol with a smaller mean diameter.

4.3 Filtration

4.3.1 Collection Efficiency of Filters

The collection efficiency of the glass fiber filters was determined by using two filter cassettes in series. The filters were exposed to oil aerosol from the laboratory generator for periods of time from one to several minutes depending on the aspiration rate and smoke density. For aspiration rates of up to 9 liters per minute, the collection efficiency, defined as

$$\text{collection efficiency} = 100\left[\frac{\text{mass on front filter}}{\text{mass on front filter} + \text{mass on backup filter}}\right] \quad (4.2)$$

is greater than 99%. Efficiencies are given for various flow rates are given in table 4.1. No decrease in collection efficiency with increasing filter face velocity is evident, but it may occur for much higher flow rates. For most of the front filters, aspiration in the fog-oil smoke produced an easily visible coating of oil over the entire surface of the filter. No oil was visible on any of the backup filters. Chromatograms produced from both the front and backup filters were similar in shape, indicating that the chemical composition of the collected material was similar for both cases.

Saturation of the filters occurred at much higher loadings than could be measured using the thermal desorption system. Saturated filters had oil clearly visible on the back side of the filter, and some contamination of the filter backing in the cassette housing. They were also difficult to remove intact from the cassette housing. For some filters which had enough collected oil to overload the chromatograph, only a measured section of the filter was analyzed in order to remain within the linear operating range of the chromatograph system.

4.3.2 Desorption Efficiency of Filters

The oil collected on the glass fiber filters is mechanically removed from the air. No chemical bonding between the oil and the glass fiber occurs. Doping filters with known quantities of oil and then analyzing them is similar in nature to the collection of aerosol on the filters. The analysis of doped filter

Table 4.1 Filtration Efficiency of Glass Fiber Filters

flowrate	filter	collected oil		percent
	face	front	backup	efficiency
(liters/	velocity	filter	filter	
min)	(cm/min)	(mg)	(mg)	(%)
0.63	140.0	0.55	0.001	99.8
1.09	240.0	12.70	0.022	99.8
3.30	730.0	2.30	0.002	99.7
6.00	1330.0	5.86	0.035	99.4
7.90	1750.0	3.20	0.042	99.8
9.07	2000.0	16.10	0.003	99.9

Average efficiency = 99.7 ± 0.1

papers indicates that the desorption from the filters is complete. Desorbed quantities compare well with the calibration results.

The fraction of oil that remains vapor through the generation process and is not collected as aerosol on the filters, but is injected onto the doped samples is insignificant, and does not appear to affect the results. In addition, sequential analysis of the same filter indicates that all of the oil is desorbed during the first analysis.

4.4 Adsorbent Tube Samplers

4.4.1 Vapor Sampling

The collection efficiency of the Tenax-GC sampling tubes when sampling vapor was measured using two sampling tubes in series. The tubes were connected together using a short section of silicon rubber tubing. An empty tube was mounted in front of the first sample tube. A sample of n-dodecane (C12) was placed in the empty tube and warmed to vaporize it while the series of tubes was aspirated to carry the vapor onto the adsorbent. The breakthrough volume was determined by interchanging backup tubes at intervals of two to three minutes, then analyzing the backup tubes to determine the time at which breakthrough occurred.

The breakthrough volume for a given adsorbent generally increases with increasing molecular weight of the sample vapor. Since n-dodecane is slightly lighter in molecular weight than any of the constituents of fog oil, results obtained using it should give a lower bound for breakthrough volume of the fog oil vapor because both are chemically similar.

In tests at flow rates of 0.25 liters per minute, no breakthrough of the n-dodecane occurred within a 30 minute aspiration time. At an aspiration rate of 0.66 liters per minute, sample breakthrough of 1.7% occurred at 23 minutes of aspiration. This would correspond to a breakthrough volume of about 15 liters for this adsorbent - vapor combination. For higher flow rates through the adsorbent tubes, a fraction of sample could be detected on the backup adsorbent tube within minutes. This is because the short residence time of the sample within the tube at higher flow rates does not allow enough time for diffusion from the sample stream to the surface of the adsorbent. Sample passes entirely through the adsorbent without being absorbed. Results at these higher flow rates are not quantitative.

4.4.2 Aerosol Collection Using Sampling Tubes

For the measurement of the collection efficiency of fog oil on adsorbent tubes, a series of two adsorbent packed tubes were exposed to the smoke from the laboratory generator. Collection efficiency was measured at several flow rates. The results from this test indicate that oil is present at small but detectable levels on the backup sampler within several minutes of the start of aspiration even at low flow rates. The adsorbent packing in the tubes behaves like a filtration device. No indication of any behavior indicating a breakthrough volume was evident from the test results. The collection efficiencies measured for the adsorbent tubes were 98% ±2% for aspiration rates from 0.68 to 1.4 liters per minute. The errors in the measurement of collection efficiency were primarily due to variations of background interference levels on the Tenax tubes prior to exposure and the subtraction errors due to corrections for this level. Measurement of aerosol collection efficiencies using a Tenax adsorption tube backed by a filter cassette produced results in the same range.

4.4.3 Desorption Efficiency of Adsorbent Samplers

The desorption efficiency of the adsorbent samplers was measured by sequential analyses of the same sample tube. Fog-oil smoke from the laboratory smoke generator was adsorbed onto several aspirated samplers. Each tube was then desorbed such that the purge flow through the tube in analysis was either in the opposite direction of the aspiration during exposure or in the same direction. This method indicates that the desorption efficiency of the Tenax-GC is 99% after the first desorption and

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independent of sampler orientation. Conditioning of the sample tube for about forty minutes after the analysis was is necessary to completely remove the remaining fog oil from the adsorbent.

In another test, adsorbent sampler tubes were doped with fog oil and analyzed so that the oil sample would be desorbed directly into the gas chromatograph during analysis. Desorption of the sample in this case was complete. In another test the tubes were again doped with oil and analyzed so the oil sample would pass through the adsorbent bed during the analysis. Desorption efficiency for the first analysis of the sample in this orientation was 50%. This increased to 67% by the second analysis, with only trace amounts of oil being desorbed in succeeding analyses of the same tube.

The low desorption efficiency for the first analysis indicates that there is significant retention of the oil by the Tenax-GC as the band of sample passes through the adsorbent during the purging of the sample tube and additional desorptions indicate some of the sample was permanently retained on the adsorbent. This did not occur in the test described in the last paragraph in which aerosol was aspirated onto the sample tube. This indicates that the desorption or vaporization mechanisms are not the same for doped sample tubes and sample tubes which have been used to collect an aerosol oil sample.

For more volatile compounds such as n-dodecane, desorption is complete after a single analysis. The incomplete desorption of the fog oil and the extensive conditioning necessary after each exposure are due to the high boiling point and low vapor pressure of the fog oil constituents. Desorption of the Tenax-GC at higher temperatures than already are being used to increase the desorption efficiency is impractical because the adsorbent will decompose or polymerize with the oil sample at higher temperatures.

4.5 Verification of Concentration Measurements using Adsorbent Samplers and Filters

In an effort to validate concentration measurements using Tenax sample tubes and glass fiber filters, a larger 21 cm diameter by 45 cm long exhaust port was added to accommodate a greater number of samplers. An array of rotameters was erected so that the individual flow rates through multiple samplers could be simultaneously monitored. Variable flow restrictors were fitted to each rotameter so that the flow rate through each sampler could be individually adjusted.

4.5.1 Correlation Between the Sampling Methods at the Same Flow Rate

In the first series of tests several adsorbent tubes and several filters were aspirated at the same flow rate, for the same time interval during each run, in the fog oil aerosol produced by the smoke generator. Comparisons of the mass concentrations calculated from the analysis of these aspirated samples showed very good correlation of the results between samplers and sample types over a range of flow rates between 0.7 to 1.4 liters per minute.

It was found necessary to correct for the background level on the adsorbent tubes in order to correlate the results for this and other tests. Analysis of a group of unaspirated Tenax samplers from the batch used in this test gave a background level of 0.83 mg, and a standard deviation of 0.15 mg. Most of the differences in filter and adsorbent tube measurements are due to this background level on the adsorbent tubes. Concentration measurements agree very well once this correction is made.

4.5.2 Correlation at Different Flow Rates

If fog oil concentrations are found to be independent of the sampler flow rate, effects such as anisokinetic sampling and the variation of collection efficiency with flow rate can be neglected. In tests on the aspiration of filter samplers at different flow rates in the same fog oil aerosol exposure, concentration measurements produced results within ±5% over the aspiration range of 1.4 to 11.2 liters per minute. This shows that collection efficiency is not a strong function of flow rate for these samplers and the fog oil aerosol.

Similar tests for Tenax adsorbents tubes produced similar results to those for the filters. The adsorbent tubes cannot, however, be aspirated above several liters per minute because of the excessive pressure drop across the adsorbent packing. In further tests with filters and adsorbent tubes, the filters were aspirated at high (11.2 liters per minute) flow rates and the adsorbent tubes were aspirated at moderate flow rates (1.2 liters per minute) in the same exposure to fog-oil smoke. Results were again in the same error band of ±5%.

4.5.3 Evaporation of Oil from Samplers

In the measurement of atmospheric concentrations of fog oil in a smoke plume, the samplers are only intermittently exposed to the aerosol because of wind turbulence. Samplers are necessarily aspirated for long periods of time to get time-averaged concentration measurements. Evaporation of oil from the samplers during this period can lead to errors in the time-averaged concentration measurements.

To test for evaporation a set of 8 samplers were aspirated in the fog oil smoke for a given period. After this period of exposure, 4 of the samplers were stored and the rest were aspirated at high flow rates in clean air. A difference in the quantity of oil measured in analysis of the set of samplers would indicate that evaporation occurred.

In the test of evaporation from filters, 25mm cassettes were aspirated at 1.8 liters per minute for thirty minutes. A set of the samplers were then aspirated at 11.2 liters per minute for an additional hour in clean air. In the analysis of these samplers, virtually no differences were found in measured amounts of oil, indicating that no evaporation occurred. In preliminary tests on adsorbent tubes, samples were aspirated for twenty minutes at a flow rate of 1.3 liters per minute. Then a set of the samples were aspirated in clean air for 60 minutes at 2.5 liters per minute. Upon analysis of these samples nearly 15% of the oil was found to have evaporated during the clean air aspiration period.

In repeated tests, it was found that aspiration in clean air at this flow rate for an additional period beyond 60 minutes produced no further loss of oil. Evaporation appears to reach an asymptotic amount of around 15% of the original sample.

Because of the limited resolution of the chromatographic analysis especially at higher levels of oil, it is impossible to determine if there is preferential retention of oil constituents on Tenax depending on the molecular weights of the components. It is likely, however, that the loss of oil is greater for the more volatile constituents.

4.5.4 Storage Losses from Filters

4.6 Field Sampling Tests

4.6.1 Description of Dugway Dosage Data

For samples collected at Dugway Proving Ground in 1985, good dosage data were collected for three tests out of eleven. The full scope of this study is discussed by Liljegren et al. (1988). The samplers used in these tests were vapor sampling tubes packed with Tenax adsorbent. The material collected on the samplers was both aerosol and vapor. For calculation of the mean concentration of oil collected at a dosage sampler in this test, the mean background was first subtracted from the analyzed mass of sample, then the result was multiplied by a linear calibration factor.

The major problem in the use of the Tenax sampling tubes for sampling the oil was the high background level of the dosage tubes. This amounted to an average equivalent to 0.47 mg of oil with a 0.19 mg standard deviation. Using a minimum level of 2σ above the average background as the criterion for the minimum detectable level of oil, gives a minimum required dose of 0.38mg of oil for detection at a 6

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dB signal to noise ratio. Coupled with the scatter in the background level was a low aspiration rate which severely limited the minimum detectable concentration. As a result, for the Dugway Dosage data, the concentration was measured out to only several hundred meters downwind from the source.

The high background level on the samplers, in hindsight, could be circumvented by more careful preparation and conditioning of the samplers prior to use, and more careful storage after exposure. In laboratory tests after the Dugway dispersion tests, it was found that the background level on the Tenax sample tubes could be kept to a minimum for several weeks by careful conditioning of the sample tubes, and storage in sealed glass tubes both before and after exposure prior to analysis. Undertaking this procedure for all of the several thousand samplers needed in a field test, with the present conditioning apparatus, would require several thousand hours.

4.6.2 Description of Camp Atterbury and Meadowbrook Dosage Data

Other dispersion tests using fog oil smoke have been conducted at Camp Atterbury, Indiana in October and November, 1987 independently, and at the Meadowbrook test site near Red Bluff, California in September and October, 1987 as a part of project WIND. Several other tests were run from June through August in 1986, at a second dispersion site within Camp Atterbury.

At Camp Atterbury in 1986, we failed to get much dispersion data suitable for model evaluation, mainly due to a poor choice for a test site and also due to unfavorable meteorological conditions on the few days that we ran dispersion tests. The dosage data from 1986 has been primarily used to evaluate errors in the sampling and analysis method. Four fog oil dispersion tests were completed at Camp Atterbury a year later, in 1987, and of these tests, three consist of relatively good data, with the wind direction perpendicular to the sampling lines and smoke concentrations measured across four or five downwind sampling transects. All of the Camp Atterbury tests were conducted in neutral to moderately unstable meteorological conditions.

The dispersion experiments conducted as a part of project WIND in California were undertaken at a canyon site in moderately mountainous terrain, and were conducted in both stable and unstable meteorological conditions, which correspond to downslope and upslope flow, respectively, along the sides of the adjacent mountains. Twelve tests in all were completed, and of these tests, two of five unstable tests and four of seven stable tests contain relatively good dosage data. The University of Illinois was responsible for the smoke dispersion in this experiment, while the recording of meteorological data and planning for the tests was undertaken by the U.S. Army Atmospheric Science Laboratory. The applicability of this data for model evaluations is currently unknown until we are able to evaluate the meteorological data, which we have not yet acquired from ASL.

In all of these experiments, smoke samples were collected on aspirated glass fiber filters. Mean concentrations are calculated from the mass of oil on the filter, the aspiration rate, and the duration of operationof the fog oil smoke generator.

The binderless glass fiber filters used in collecting the fog oil smoke were mounted in open-faced 37 mm polycarbonate filter cassettes with 3 inch inlet extensions (Nuclepore), and aspirated with a vacuum pump through hollow 8 meter tall masts. For the tests in 1987, either two or four filters were mounted at several heights along the masts. Up to eight filters at one meter height increments may be used with this system. The flow rate was monitored with a rotameter at each sampling mast. A significant improvement in sensitivity over the Tenax sampling tubes was possible because of an aspiration rate ten to twenty times higher than in the Dugway experiments.

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4.7 Error Analysis of the Dosage Data for Filters

4.7.1 Chromatograph Analysis Errors

Calibration runs and baseline (background) checks were made daily on the gas chromatograph over the entire analysis period. For the calibration runs, a 1μl sample (0.91 mg) was doped on a clean stainless steel tube and the sample was analyzed. Blank runs were made to determine background levels. Over the June to November period in 1986, samples analysis for the Camp Atterbury data taken in 1986 gave results of:

	mean detector counts	equivalent mass (mg)	standard deviation detector counts	equivalent mass (mg)
calibration	$9.6634(10^7)$	0.910	$1.0242(10^7)$	0.0964
baseline	$1.5049(10^4)$	0.000141	$1.0662(10^4)$	0.000100

Dosage samples from the 1987 dispersion tests were analyzed over the period from September, 1987 to February, 1988. Similar results from calibration and blank runs were recorded as follows:

	mean detector counts	equivalent mass (mg)	standard deviation detector counts	equivalent mass (mg)
calibration	$1.0478(10^8)$	0.910	$2.3502(10^7)$	0.2041
baseline	$1.0267(10^6)$	0.0089	$8.7324(10^5)$	0.0076

For a 90% confidence interval, the value measured by the gas chromatograph will be within ±17% of the actual mass of oil using the data for the 1986 calibrations. For the samples analyzed in 1987, the calibration error increased, for the same confidence interval, to ±36%. This increase was mainly due to problems in the operation of the chomatograph during the analysis period in September and October (during which the experienced chromatograph operators were still collecting field data in California). Samples analyzed in September and October have been reanalyzed (filters were analyzed in sections to permit multiple analyses) to verify or improve the earlier measurements. Neglecting the anomalous calibrations in September and October, the average detector count becomes 1.1065 (10^8) and the calibration error decreases to ±15%, which is consistent with the error measured during the 1986 analyses.

The significant change in background level between the two analysis sets taken in 1986 and 1987 is due to a slightly shorter analysis cycle time in the later analysis sets, and increased column background levels over the life of the column. The increase in background level on the chromatograph, while significant, is not yet a problem for the typical sample size analyzed in our dispersion tests.

A minimum level of 2σ above the average background was used as a criteria for the minimum detectable level of oil. This corresponds to a 0.0152 mg oil sample in the chromatograph and a 6 dB signal to noise ratio. With only half fractions of filters actually analyzed, the effective minimum detectable mass of oil is 0.03 mg on the field samples.

4.7.2 Sampling Errors and Other Sources of Error

Several types of error may be present in the measured dosage using the filter samplers. These errors are examined in the following sections, and include losses due to the sampling geometry, the volatility of the oil, losses of the oil over the period of storage prior to analysis, and errors in the measured aspiration flow rate.

4.7.2.1 Flow Rate

The aspirated flow rate was monitored in our field tests with a rotameter mounted between the vacuum pump and the filter support mast. With this flow geometry, the inlet of the rotameter is not at atmospheric pressure, for which the flow meter is calibrated, but at some lower pressure dictated by the flow resistance of the filter cassettes.

This bias error in the measured flow rate Q may be adjusted by compensating for the density of the fluid ρ in the rotameter, according to Miller (1983) by:

$$Q_{actual} = Q_{design}\sqrt{\frac{\rho_{design}}{\rho_{actual}}} \qquad (4.3)$$

or, using the ideal gas equation of state:

$$Q_{actual} = Q_{design}\sqrt{\left[\frac{T_{actual}}{T_{design}}\right]\left[\frac{P_{design}}{P_{actual}}\right]} \qquad (4.4)$$

where T and P are both in absolute units. Design conditions for this rotameter are standard atmospheric conditions, or 25°C and 1 atm. In laboratory measurements of the pressure corrections. for 4 glass fiber filters mounted on a single mast:

Flow rate each filter (liters/min)	Pressure ratio P_{design}/P_{actual}	correction factor Q_{actual}/Q_{design}
11.85	1.038	1.018
17.8	1.059	1.029
23.7	1.091	1.045

For two filters mounted on a single mast:

Flow rate (each filter) (liters/min)	Pressure ratio P_{design}/P_{actual}	correction factor Q_{actual}/Q_{design}
23.7	1.073	1.036
35.5	1.125	1.060
47.4	1.177	1.085

Temperature corrections to the flow rates can be applied using the average ambient temperature for the period of the test. In the more severe conditions encountered in our field tests this amounts to an error of less than two percent.

The flow rate through each sampling mast was set at the beginning of each test and remained constant over the duration of the test. There was no evidence of reduced flow rate over the duration of the test, both because the actual mass loading on each filter was small, and because the fiber filters do not clog as easily as membrane type filters.

4.7.2.2 Aerosol Sampling Losses

In sampling of aerosols, losses of particles before they are collected on a filter may occur due to gravitational settling, inertial forces (anisokinesis), diffusion, or electrostatic forces. For atmospheric aerosols in the $0.1\mu m$ to $4\mu m$ size range, which encompass 99% of the particle size range for fog oil droplets (on a mass basis) in our experiments, electrostatic and diffusion losses are negligible. It is necessary, however, to further quantify any inertial or gravitational settling losses which may occur for this aerosol.

4.7.2.2.1 Inertial Particle Losses

Inertial losses of particles may occur in aerosol sampling due to the inability of the particles to identically follow the flow field near the sampler inlet for conditions when the flow is accelerated or decelerated. This may cause the measured concentration to be either larger or smaller than the ambient aerosol concentration. For inlets aligned into the flow direction, inertial losses will be eliminated if the face velocity, V, at the inlet is equal to the external flow velocity, W. For conditions where this does not occur, the collection efficiency will be a function of both the velocity ratio W/V, and the particle Stokes number, given by:

$$St = \frac{C_s D_p^2 \rho_p V}{9v D_s} \qquad (4.5)$$

where C_s is the Cunningham slip correction factor, D_p is the particle diameter, ρ_p is the particle density, v is the kinematic viscosity, and D_s is the inlet diameter of the sampler. The Stokes number physically represents the ratio of the particle stopping distance to the characteristic probe dimension. The particle stopping distance calculated in this manner is valid only when the drag on the particle is in the Stokes flow regime, which includes only very small Reynolds numbers (based on the particle diameter). The collection efficiency for probes with this orientatation have been experimentally investigated by Belyaev and Levin (1974) and Davies (1968). In general their results show the collection efficiency has greater deviation from unity for increasing Stokes numbers.

For inlet geometries where the probe is oriented at an angle relative to the external flow velocity, the collection efficiency is a function of the probe angle as well as the velocity ratio W/V, and the particle Stokes number, St. This effect has been investigated by Durham and Lundgren (1980), and Tufto and Willeke (1981). For this sampling geometry the collection efficiency generally decreases with increasing angle between the probe inlet and the approaching flow.

In field experiments, the sampler orientation with respect to the wind direction is constantly changing and the velocity ratio W/V also is not steady. Corrections to the data from wind tunnel tests could not be made without a great deal of inherent error. The only hope of avoiding collection efficiency problems due to this effect is in selecting a sampling geometry which minimizes inertial losses of particles by operating in a range with a small Stokes number.

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For the fog oil aerosol, (ρ_p = 0.91 g/cm^{-3}), typical values of the particle stopping distance (in cm) are as follows:

Flow velocity, W → particle diameter ↓	1 m/s	2 m/s	5 m/s	10 m/s
0.1 µm	3.531(10^{-6})	7.620(10^{-6})	1.790(10^{-5})	3.531(10^{-5})
1 µm	3.083(10^{-4})	6.166(10^{-4})	1.541(10^{-3})	3.083(10^{-3})
4 µm	4.939(10^{-3})	9.878(10^{-3})		

Values are not calculated for the blank areas of this table because the flow around the particle is no longer in the Stokes flow regime.

The largest Stokes number found from this table and using our filter cassettes with a 3.7 cm diameter inlet, is St = 2.66 (10^{-3}). This value is much smaller than any cited in the previously mentioned papers. Therefore, no quantitative estimate of collection efficiency is made here because extrapolation of the experimental data would be necessary. Davies (1968) cites a conservative upper limit for the Stokes number, such that for St < 4 (10^{-3}) there are no sampling losses due to inertial effects. The greatest fraction of particles and wind speeds in our tests met this criterion.

4.7.2.2.2 Gravitational Settling Losses

In gravitational settling, collection efficiency may be affected by the finite downward velocity, v_s, of the particles. This is a more significant problem with larger aerosol particles. In stagnant air, the settling velocity of a particle is the terminal velocity of a particle for which the aerodynamic drag on the particle is equal to the gravitational force. Typical calculated values for the fog oil smoke are as follows:

particle diameter	Settling velocity (cm/sec)
0.1 µm	3.152(10^{-5})
1 µm	2.750(10^{-3})
4 µm	4.409(10^{-2})

Evident from these values is the fact that for particles in the size range of fog oil smoke particles, the settling velocity is very small. This velocity is typically nondimensionalized by the flow velocity, W, as

$$V'_s = \frac{v_s}{W} \qquad (4.6)$$

Settling losses are more significant for larger V'_s, so that these effects are greater in stagnant conditions. Davies (1968), cites a conservative upper limit on the nondimensionalized settling velocity of $V'_s < 4(10^{-2})$ which, if met, insures that gravitational settling is an insignificant effect relating to collection efficiency. For the 4µm particle size in the above table, this corresponds to a minimum acceptable wind speed of about 1 cm/s, which is met for nearly all conditions in the atmosphere.

Agarwal and Liu (1980) specify a criteria for at least 90% collection efficiency for conditions when the product (St)(V'_s) < 0.1. This criteria is easily met for all of our sampling conditions. In summary, then, there is a good theoretical basis for assuming that the collection efficiency of our samplers is not affected by inertial effects or gravitation setting of the aerosol particles.

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4.7.2.2.3 Experimental Considerations of Particle Losses

To further quantify any losses in sampling efficiency for the fog oil smoke, a diagnostic field tests was run at Camp Atterbury on July 9, 1986. In this test, sets of sampling masts were located in groups of four downwind from a fog oil generator. The masts in each group of four were set up such that:

1. A mast was oriented so that the open face of the filter cassettes faced into the wind, toward the smoke generator. This is the ideal sampler orientation and was used in our full scale field tests.

2. Another mast was oriented 180° relative to mast No. 1 so that the open face of the filter cassettes faced downwind. This was done to investigate the worst possible effects of inlet losses due to sampler inlet geometry.

3. A third mast was oriented the same as No. 1, but aspiration continued for 30 minutes after the smoke generator was shut off. This was to investigate any evaporation of oil from the filters under extended aspiration.

4. A fourth mast was oriented the same as No. 1, but was aspirated at 11.8 liters per minute or at half the flow rate of the other three masts, which were aspirated at 23.6 liters per minute. This setup was intended to estimate the errors due to inlet effects and also due to filter collection efficiency. Additional errors could also occur due to errors in the calibration of the flow meters at the different flow rates.

Two sets of four masts were hit by smoke in the test, each mast had a filter cassette at the 2, 4, 6, and 8 meter level. The results were as follows:

location   Filter setup, (measured concentrations are in mg/m^3)

mast & height	(1)	(2)	(3)	(4)	avg	σ	σ/avg
4, 2	*20.4*	12.3	16.5	18.2	16.85	2.96	0.175
4	18.2	13.0	17.8	*18.8*	16.95	2.30	0.136
6	16.5	16.8	10.5	*19.5*	15.82	3.29	0.207
8	9.06	7.83	7.78	*13.9*	9.64	2.51	0.260
3, 2	6.32	*8.74*	6.46	failure	7.17	1.10	0.153
4	6.06	*8.35*	8.26	–	7.56	1.06	0.140
6	*4.71*	3.35	4.31	–	4.12	0.57	0.138
8	3.01	3.31	*4.16*	–	3.49	0.49	0.140

The maximum concentration measured at each location is indicated in italics within the table for a particular grouping of samplers. Agreement in measured concentration is fairly good for all these groups of samplers. Corrections to the flow meter readings based on the absolute pressure just upstream from the flow meter have been applied to the above data.

For all of the sampler geometries, no trend is evident and we can assume the effects that these setups were intended to investigate are negligible. The total error in the above set of measurements taken as a group is <standard deviation/mean≥ 0.169, or with a 90% confidence interval, ±28%.

4.7.2.2 Storage Losses

4.7.2.2.1 Oil Losses From Field Samples

In the 1986 dispersion experiments, many months were required for the dosage sample analysis. This meant that some filters were stored for a considerable period of time before they were all analyzed. Loss of oil were found to have occurred on these samples. For a July 3, 1986 test, we returned to the laboratory from Camp Atterbury and several filter samples (sections of the filters) were analyzed that evening to determine if any oil had been collected during the field test. These samples were from the even height increments of 2, 4, 6, and 8 meters on sampling mast number 12 and a single sample from mast 6. The other remaining samples from this test were finally analyzed on November 1-5, 1986, and the remaining sections of the already analyzed filters were reanalyzed. The results from the filter sections analyzed in both November and July are as follows:

sample	mass (mg)		concentration (mg/liter or mg/m^3)		fractional mass change
	(July) x1	(November) x2	(July)	(November)	(x2-x1)/x1
m.6s.2	1.848	1.020	3.730	2.060	0.447
m.12s.8	5.813	4.906	11.70	9.900	0.156
m.12s.6	5.753	4.206	11.60	8.489	0.268
m.12s.4	4.302	3.262	8.680	6.583	0.241
m.12s.2	3.800	2.618	7.667	5.284	0.311

The average loss on reanalyzed filters was 28.28% with $\sigma = 0.0956\%$.

Another check was made by analyzing the filters at the 1, 3, 5, and 7 meter height on mast 12 in November to compare with the results obtained for the 2, 4, 6, and 8 meter heights in July. Since the gradients was not evident along an 8 meter mast for any of the field samples taken in this unstable dispersion test, the values at each of the height locations on the mast should be very close to each other. Comparisons with the reanalyzed filter segments are also made in the following table. The average values obtained were as follows:

Analysis	averaged over	mean samples	standard deviation (mg)	(mg)
July	8,6,4,2	4.915	0.876	
November	8,6,4,2	3.748	0.875	
November	7,5,3,1	1.152	0.078	

Losses:

(x1-x2)/x1   reanalyzed = 23.74%
              unanalyzed= 69.35%

This shows that a much greater amount of oil was lost from the unanalyzed filters than from those that were reanalyzed. One explanation may be that for the unanalyzed samples, the oil was wicked from the filter onto the porous cellulose fiber backup disk, while the unused filter sections for the samples which were reanalyzed were stored loosely in the cassette holders and not in intimate contact with the backup disks. The samples stored for long periods in other tests with the filter in contact with the backing

disk would be expected to have losses around 70%, the same as the unanalyzed filters in the above example.

4.7.2.2.2 Comparison with Real Time Sampler Data

Several data records were taken with a GCA aerosol photometer which measured the light scattered from a volume of aerosol in the smoke plume for the 1986 Camp Atterbury tests. By calibrating this instrument in the laboratory with fog oil smoke and analyzing the dosage samples concurrently taken during the calibration with the gas chromatograph, an independent check on the dosage values obtained in field tests can be made. The gas chromatograph analysis of filter samples taken in these lab tests was completed soon after the test to minimize losses due to storage of the samplers. From this calibration, errors due to losses of oil from the filters during storage can be estimated.

For a 30 minute exposure to fog oil smoke in a laboratory smoke chamber, with the instrument aspirated at 3.5 liters per minute, the following values were measured:

Gas Chromatograph Dosage (mg)	Real-time instrument Concentration (mg/m^3)	Mean (mv)	Standard error (mv)	Conversion mg/(mv m^3)
1.29	12.3	311.3	135.8	0.0395
0.82	7.80	203.1	83.9	0.0384
0.67	6.37	135.4	55.2	0.0470

The mean dose compares favorably with a gross estimate of 19.5 mg/m^3 mean concentration of fog oil aerosol estimated from bulk flow of oil and air in the exposure setup, but it is still low. The gross estimate of concentration may be in error because of diffusion and settling losses in the fog oil smoke delivery tube and also because of the variability in flow rate through the plenum.

For test 2 on August 8, 1986 the GCA mean voltage level over the period of the test was 101.89 mv, or, with the above response factor, 4.02 mg/m^3. Adjacent masts number 35 and 36 measured a concentration of 0.8038 and 0.7234 mg/m^3 (.769 and .692 with flow correction). These values are lower than the GCA estimate by 81.0%.

For test 2 on August 7, 1986 the GCA mean voltage level was 273.211 mv. With the above scaling factor, this becomes 10.79 mg/m^3. Mast 1, which was near the GCA instrument, gave a concentration of 1.585 mg/m^3. In this case the concentration was low by 85.0%.

4.7.2.2.3 Laboratory Tests of Oil Losses on Extended Storage

In an attempt to duplicate the losses due to extended storage of samples before analysis, some laboratory tests have also been made. In these tests, sets of 28 filter cassettes were simultaneously dosed with fog oil smoke in a laboratory setup consisting of a small smoke generator and a well mixed aerosol chamber in a continuous flow setup. These filters were all aspirated at the same flow rate and should all have the same dose of oil within a group. Any differences in dose upon analysis can be attributed to losses in storage. Several sets of filters were dosed with oil and stored in various ways, some to duplicate previous methods of storing the samples, and some to find better ways of storing the samples in future field tests. These methods were as follows:

A. The dosed filters were kept in filter cassettes without separating them from the backup support, in the same manner as most of the 1986 and 1987 Camp Atterbury samples were stored.

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B. The filters were separated from the backup support, but kept loosely in the original filter cassette for storage. Most of the Meadowbrook samples taken in 1987 were stored in this manner.

C. The filters were removed from the cassette holders after exposure, cut, and folded into a stainless steel tube which was capped with plastic end caps.

D. The filters were prepared as in C but instead of plastic end caps, the stainless steel tubes were stored in clean glass screw top culture tubes. Since only sections of the filter could fit into the stainless steel tubes, the filters used here were from the same set as in C.

Simultaneous measurements of real-time smoke concentration were taken for the above tests. Autocorrelations of the data in all cases decayed to zero in 5 seconds. The duration of all tests was 30 minutes. The error in dosage over the thirty minute test can be found using

$$\frac{\sigma_E}{E} = \frac{\sigma_\theta}{E\sqrt{N}} \tag{4.7}$$

where N is the number of independent samples taken during the test, E is the mean level, σ_θ is the standard deviation and s_E is the error in the mean. N can be estimated from the autocorrelation and the sampling time (Bendat and Piersol, 1971). For the tests, these values from the real-time sampling instrument were:

Test	E(mv)	σ_θ(mv)	σ_E/E
A	238.6	72.3	1.6%
B	215.2	42.5	1.04%
C & D	216.2	12.8	0.31%

so that the error in total dosage on the filters should be small.

The data for the mass of oil measured on the filter versus the time between exposure and analysis is presented in figure 4.4. The data in these graphs indicate progressively less scatter in the data for storage methods A through D. For each set of data over the entire period, the statistics of the data are given by:

Test Setup	σ/mean	error
A	0.565	±95%
B	0.287	±48%
C	0.104	±17%
D	0.374	±16%

The error quoted in this table corresponds to a 90% confidence interval.

For case A, a few of the filters analyzed after long storage times had losses similar in magnitude to those found for the field samples taken in 1986. There is also considerable scatter in the data which creates a problem in finding a correction factor as a function of storage time. For extended storage of samples, as occurred for samples taken at Camp Atterbury in 1986, a correction factor of 5, corresponding to an 80% loss of oil is appropriate. All of the samples taken at Camp Atterbury in 1987 were also stored in this manner and a similar correction factor is appropriate.

The filters from the Meadowbrook dispersion tests were stored the same as filters in case B. While the storage losses are less than in case A, they are still considerable and need correction.

It is notable that the error for setup C and D is very close to the standard error in determining the mass of oil with the gas chromatograph alone. Since the gas chromatograph error is included in the above figures, almost no additional error can be attributed to storage losses in these cases. The problem in storing filters in this manner is only in the time and labor required to pack the filters in the storage tubes. In field situations, where a quick turnaround time is required for the next day of testing, and hundreds of dosage samples are taken in each test, we simply lacked the personnel to use either of these methods.

4.7.2.3 Losses on Meadowbrook Samples

For a single test, on September 23, 1987, in the Meadowbrook field studies, the filters were cut in half and one set was stored loosely in the cassettes as in case B, while the other half was stored identically to case D. The average of the mass ratios measured for each sample fragment under the two different storage methods gives a good correction factor since the losses in case D are negligible. The ratio of values in this case is 3.1, which amounts to a loss of 68% of the oil. This is consistent with the laboratory tests in that the measured value shows less oil loss than filters stored as in case A.

4.7.2.4 Conclusions on Dosage Data Errors Attributable to Sampling and Analysis for Filter Samplers

Most sources of error in the sampling and analysis method for fog oil have been investigated. Of these errors, the bias error due to oil loss in storage of the samplers between exposure and analysis overwhelms other sources of bias error. For example in comparison of cassette filters with similar doses of oil analyzed more than several months apart, a loss of 70% of the oil was found for samples both in 1986 field experiments and in later laboratory tests. In comparison of a calibrated real-time sampler with dosage values for the same field experiments, losses were in the range of 81% to 85%.

Further work has shown that when a correction factor of five was applied to the Camp Atterbury data taken in 1986, agreement between simple Gaussian plume models and the data was within a factor of two. This agreement can be considered to be very good.

In the laboratory experiments, other methods for storing the filters before analysis were investigated. An improved method of storing the samples which requires packing the filter into a stainless steel sampling tube after exposure showed no storage losses. Packing the filter loosely in the filter cassette showed moderate losses, with much less labor in preparation required than the stainless steel tube storage.

For the 1987 field experiments, the Camp Atterbury samples were stored in the same manner as in 1986, and the same storage loss factor of 5 for bias error is applied to this data. The Meadowbrook samples were stored loosely in the filter cassettes, and the storage loss factor applied to this data is 3.1 which corresponds to a slightly smaller loss of oil.

The major reason for not storing all of our filter samples using a method found to have no losses was the time required to physically store them in this manner. In generating several hundred samples per test, the task could not be accomplished before the next scheduled test.

To minimize the relative bias error between dosage samples for a single test, the group of samples taken in a particular test were analyzed together. Analysis of a single set of samples could be completed in about six long days. In this way, a single correction factor could be applied to all the data for a given test, and while the absolute mass in each case is subject to a degree of error, the relationship between relative dosages in a test is still maintained.
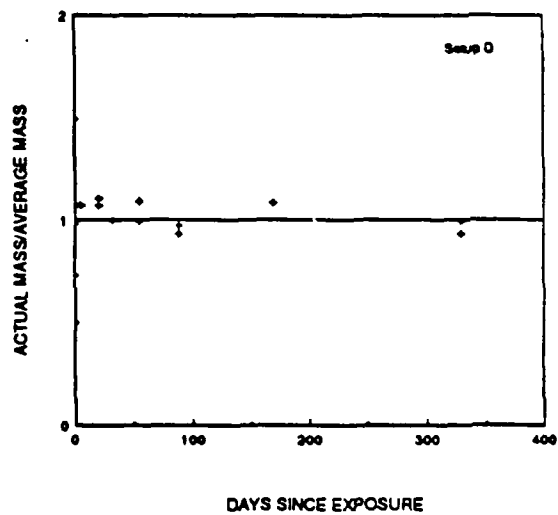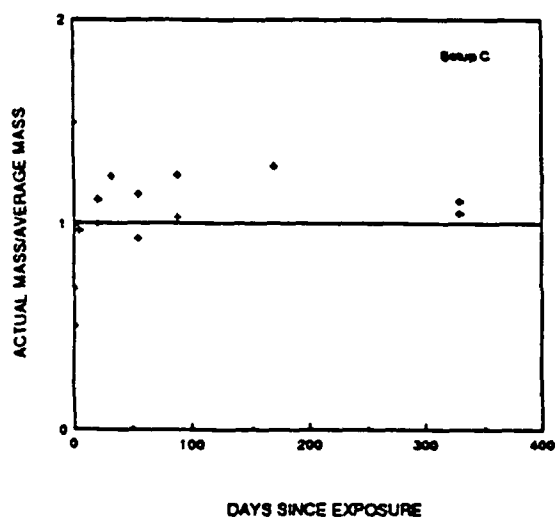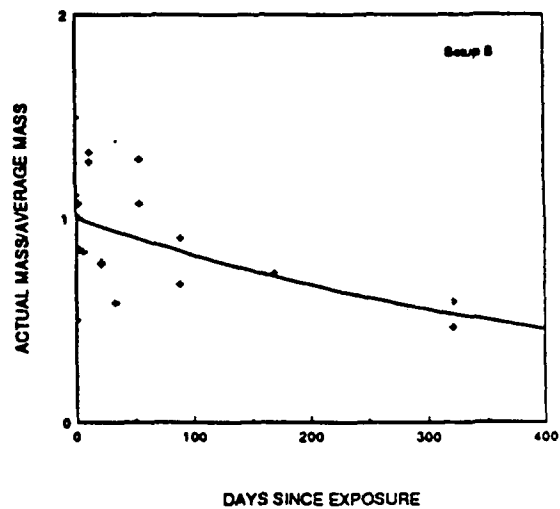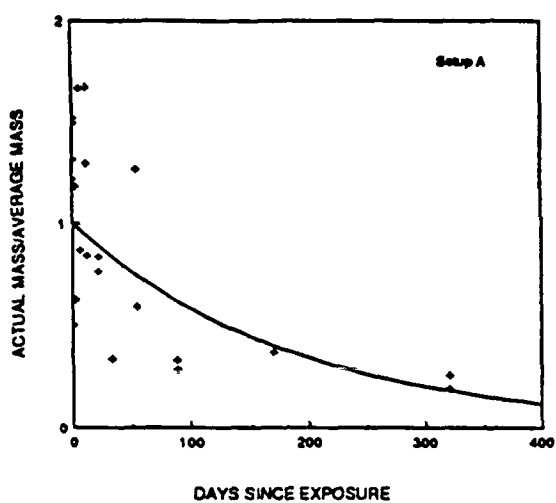
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Figure 4.4 Oil Losses from Filters for Several Different Storage Methods.
A Complete Description of Each Method is in the Text.

The standard error for samples analyzed with this method can be estimated from the large group of laboratory samples which were each dosed with an identical mass of fog oil smoke. For this purpose, the samples analyzed at very long storage times were neglected, giving an estimated error of

Test Location:	σ/mean	error
Meadowbrook	0.24	±40%
Atterbury	0.38	±60%

for each test. This error does seem large in comparison with other more common engineering measurements, but the difficulty in analyzing these samples is that the analyzed quantities are extremely small. A one milligram sample of oil collected on a filter over an hour test period at a flow rate of 17 liters per minute, which is reasonable for these field studies, corresponds to a concentration of only about one part per million, on a mass basis.

5.0 CONCLUSIONS

For the purpose of determining the downwind concentrations of smoke from an oil fog generator it was necessary to develop a sampling and analysis method for quantifying an oil fog smoke. The speed of analysis, minimal manual sample preparation, accuracy and sensitivity of measurements, and the ability to handle a large number of samples were the primary criteria for selecting this method.

A review of analysis techniques for pollutants and atmospheric tracers indicated that thermal desorption of atmospheric samples required less sample preparation than liquid extraction or other methods and presented fewer opportunities for the introduction of errors in the analysis.

Previous work with thermal desorption focused on the collection of volatile vapors on a solid adsorbent. Collection of samples of oil fog smoke, consisting of both vapor and liquid fractions, on the tenax adsorbent samplers did not give desirable results, mainly due to the contamination of the samplers and the resulting high background levels.

Glass fiber filters were found to perform better for the collection of fog oil smoke than adsorbent samplers because the filters are less susceptible to contamination. The filters could also be analyzed by the same thermal desorption method, with the collected oil being simply vaporized from the filter.

The high boiling point of the oil presented some problems in the design of the desorption system. Previous systems had been primarily used for the desorption of volatile vapors. The entire sample path needs to be heated to avoid condensation of the oil and contamination of the system. Desorption of samples in the chromatograph injector eliminated the condensation problem. This system proved to be fairly reliable and easily maintained throughout a large number of analyses.

The desorption system may also have application in the analysis of polyaromatic hydrocarbons (PAH) which are part of the ambient aerosol. Many of these compounds are potent carcinogens. The atmospheric concentration of these compounds is conventionally measured by solvent extraction of an aspirated filter with gas chromatographic analysis of an aliquot of the solution. Thermal desorption of the filter would eliminate manual steps and reduce the cost per analysis. The applicability of thermal desorption to PAH compounds depends on the volatility and boiling point of the chemical under study.

Determination of quantities of oil down to 0.01 mg is possible using this method. Other methods, primarily utilizing the fluorescence of the oil have a similar minimum detection level (NIOSH P&CAM 159, 1977), but require more sample handling and preparation prior to analysis.

Interferences are primarily due to background levels of contaminants present on the filters and sample tubes. The addition of a unique tracer material to the oil fog to aid detection by electron capture detection may also be of use in extending the detection limit of the smoke. A chemical similar to DCBP as used by Jenkins et al. (1983) would be desirable. The problems in finding a suitable tracer at a reasonable cost that is safe and performs adequately are significant.

In conclusion, the use of glass fiber filters for sampling and thermal desorption analysis provides an effective and fast method for quantifying oil fog smoke samples for a large number of samples, while absorption tubes are less desirable because of their tendency to become contaminated. The analysis method is applicable over a wide range of sample sizes and ambient concentrations. It is suitable for the determination of concentrations of oil fog smoke downwind from a generator in field studies.

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